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MEXAMS--THE METALS EXPOSURE ANALYSIS MODELING SYSTEM

by

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MEXAMS, the Metals Exposure Analysis Modeling System, provides an enhanced capability for assessing the impact of priority pollutant metals on aquatic systems. It allows the user to consider the complex chemistry affecting the behavior of metals in conjunction with the transport processes that affect their migration and fate. This is accomplished by linking MINTEQ, a geochemical model, with EXAMS, an aquatic exposure assessment model. MINTEQ is a thermodynamic equilibrium model that computes aqueous speciation, adsorption and precipitation/dissolution of solid phases. It has a well-documented thermodynamic data base that contains equilibrium constants and other accessory data for seven priority pollutant metals: arsenic, cadmium, copper, lead, nickel, silver and zinc. The model was developed by combining the best features of two other existing geochemical models MINEQL and WATEQ3. EXAMS is designed for the rapid evaluation of synthetic organic pollutants. Given the characteristics of a pollutant and an aquatic system, EXAMS computes steady-state pollutant concentrations (exposure), the distribution of the pollutant in the system (fate), and the time required for effective purification of the system (persistence). Its linkage to MINTEQ required several modifications. To facilitate the use of MEXAMS, a user interactive program was developed. This program queries the user to obtain water quality data for MINTEQ, then controls the operation of MINTEQ and EXAMS, passing simulation results back and forth between the models.

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The MEXAMS computer code has been tested against other computer programs to verify its computational accuracy. Nevertheless, errors in the code are possible. The U.S. Environmental Protection Agency assumes no liability for either misuse of the model or for errors in the code. The user should perform verification checks of the code before using it.

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FOREWORD

As environmental controls become more costly to implement and the penalties of judgment errors become more severe, environmental quality management requires more efficient analytical tools based on greater knowledge of the environmental phenomena to be managed. As part of this Laboratory's research on the occurrence, movement, transformation, impact, and control of environmental contaminants, the Technology Development and Applications Branch develops management or engineering tools to help pollution control officials achieve water quality goals.

Concern about environmental exposure to heavy metals has increased the need for techniques to predict the behavior of metals entering natural waters as a result of the manufacture, use, and disposal of commercial products. A number of mathematical models have been developed to provide data on metals transport and fate from which exposure assessments can be made. The modeling technique described in this manual permits the user to examine speciation of heavy metals along with transport and fate in various aquatic systems. Because different species of a metal cause different biological effects, this model should help users better relate metals discharges to observed effects.

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ABSTRACT

MEXAMS, the Metals Exposure Analysis Modeling System, provides an enhanced capability for assessing the impact of priority pollutant metals on aquatic systems. It allows the user to consider the complex chemistry affecting the behavior of metals in conjunction with the transport processes that affect their migration and fate. This is accomplished by linking MINTEQ, a geochemical model, with EXAMS, an aquatic exposure assessment model.

MINTEQ is a thermodynamic equilibrium model that computes aqueous speciation, adsorption and precipitation/dissolution of solid phases. It has a well-documented thermodynamic data base that contains equilibrium constants and other accessory data for seven priority pollutant metals: arsenic, cadmium, copper, lead, nickel, silver and zinc. The model was developed by combining the best features of two other existing geochemical models: MINEQL and WATEQ3.

EXAMS is designed for the rapid evaluation of synthetic organic pollutants. Given the characteristics of a pollutant and an aquatic system, EXAMS computes steady-state pollutant concentrations (exposure), the distribution of the pollutant in the system (fate), and the time required for effective purification of the system (persistence). Its linkage to MINTEQ required several modifications.

To facilitate the use of MEXAMS, a user interactive program was developed. This program queries the user to obtain water quality data

for MINTEQ, then controls the operation of MINTEQ and EXAMS, passing simulation results back-and-forth between the models.

As it is currently structured, MEXAMS can be used in a number of ways. It can be used like EXAMS to perform rapid hazard evaluations for priority pollutant metals. MEXAMS can also be used to evaluate the impact of point source discharges and mine drainage as well as to support the interpretation of metals bioassay data. Finally, and perhaps most importantly, MEXAMS can be used as a framework for defining what is and what is not known about the behavior of priority pollutant metals in aquatic systems. This framework will make it possible to identify the need for and guide the performance of future research.

This report was submitted in fulfillment of Contract No. 68-03-3089 by Battelle, Pacific Northwest Laboratories under the sponsorship of the U.S. Environmental Protection Agency. The report covers the period September 14, 1981 to August 31, 1983, and work was completed as of August 31, 1983.

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SECTION 1

INTRODUCTION

As a result of the National Resources Defense Council (NRDC)/Environmental Protection Agency Settlement Agreement (as modified), the EPA is required to examine the need for more stringent effluent limitations and guidelines in order to attain and maintain acceptable water quality conditions. EPA must also examine the presence, sources, effects of, and interrelationships between priority pollutants in aquatic systems.

Given the Water Quality Criteria published on November 18, 1980 in the Federal Register, the one class of priority pollutants likely to receive considerable attention is the priority pollutant metals. One reason for this attention is the fact that the current criteria are based on "total recoverable" rather than "dissolved" concentrations. Historically, only total concentrations were reported in the published results of aquatic bioassays for metals, even though it was generally known and accepted that the dissolved fraction is the most bioavailable and toxic, and that certain dissolved species are much more toxic than others. Only recently have investigators like Andrew et al. (1977), Chakoumakos et al. (1979) and Allen et al. (1980) sought to experimentally determine the toxicity of different dissolved species.

Another reason for the growing attention is the concern that the criteria are too stringent. Industry would prefer that either the dissolved fraction or the most toxic forms be regulated so they can avoid unnecessary treatment. They and others point to the many locations where total metal concentrations exceed the criteria without any apparent ecological impacts.

The final reason is that EPA is now giving states the latitude to establish the specific standards. This move is in recognition of the major impact that local water quality conditions can have on the proportion of total metal that is dissolved and on the species that are likely to be present.

These issues have generated a need to reexamine the basis for the priority pollutant metal criteria. They have also generated a need to develop improved methods for predicting how metals will behave in aquatic systems.

To date, virtually all modeling studies directed at examining the migration and fate of metals have neglected many of the more important chemical interactions controlling their behavior in aquatic systems. In their study of Pb, Cd, Zn, Cu and S movement through Crooked Creek Watershed in Missouri, Munro et al. (1976) considered only metal adsorption through the use of an equilibrium partitioning coefficient. A similar approach was used by Raridon et al. (1976) in the study of Cd and K movement in Walker Branch Watershed in Tennessese and by De Pinto[a] et al. in their analysis

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(a) Presentation by J. V. DePinto, W. L. Richardson, and R. Wethington on Mathematical Modeling of Heavy Metals Transport in the Flint River, Michigan at the SETAC Third Annual Meeting in Arlington, Virginia on November 14-17, 1982.

of Zn, Cd and Cu movement in the Flint River in Michigan. Orlob et al. (1980) used a non-equilibrium partitioning coefficient for sediment adsorption, as well as one for dissolved organic matter, in their study of Cu movement off of the California coast.

None of these studies, however, explicitly considered metal speciation and its resultant effect on metal adsorption and precipitation, both of which act to reduce the amount of metal in solution.

These factors are explicitly considered in MEXAMS, the Metals Exposure Analysis Modeling System. It represents an improvement in metals modeling in that the complex chemistry affecting the behavior of a metal and the transport processes affecting its migration and fate are handled by two separate, but linked, models. The chemical interactions are handled by MINTEQ, a geochemical model that uses fundamental thermodynamic equilibrium relationships and data to calculate dissolved, adsorbed and precipitated metal concentrations. The migration and fate of the metal is handled by the Exposure Analysis Modeling System (EXAMS), a steady-state transport model developed primarily as a screening level model by the EPA Environmental Research Laboratory in Athens, Georgia.(b)

A similar approach was also recently taken Dr. Bernard Chapman at the Commonwealth Scientific and Industrial Research Organization (CSIRO) in Australia. Dr. Chapman linked MINEQL with his own transport model to examine the impacts of mine drainage on the quality of receiving waters (Chapman et al. 1982 and Chapman 1982). The success of his modeling studies provides considerable support to the approach taken in the development of MEXAMS.

(b) Burns, L. A., D. M. Cline and R. R. Lassiter. Exposure Analysis Modeling System (EXAMS): User Manual and System Documentation. U.S. Environmental Protection Agency, Athens, Georgia. EPA-600/3-82-023.

This report is a user's manual for MEXAMS. It is divided into four main sections. The first provides a general description of MEXAMS. Specifically, the function of each component of MEXAMS is described, as is the operation of the system. This section concludes with a discussion of the applicability and limitations of the modeling system.

The second section is a primer on key concepts in aqueous chemistry. In preparing this report it was assumed that most users would not have formal training in chemistry. For this reason, an introduction to some of the concepts important to understanding the chemistry of metals in natural waters is provided.

The third section discusses how to use MEXAMS. Specifically, it discusses the options available to the user, data requirements and how to interpret model outputs and error messages. To facilitate the use of MEXAMS, a step-by-step discussion of data entry procedures is provided.

The fourth section is a programmer's supplement. It outlines: 1) the structure of MEXAMS, 2) resource requirements for its operation, and 3) procedures for its implementation.

Before applying MEXAMS, the reader is encouraged to review MINTEQ - A Computer Program for Calculating Aqueous Geochemical Equilibria by A. R. Felmy, D. C. Girvin, and E. A. Jenne, (1983). This report presents the mathematical and chemical concepts embodied in MINTEQ. While it is not necessary to master these concepts in order to use MEXAMS, it is important that the user be familiar with the basic theory behind MINTEQ. The reader is also encouraged to review Exposure Analysis Modeling System (EXAMS): User Manual and System Documentation by L. A. Burns, D. M. Cline, and R. R. Lassiter. While not all of the capabilities of the EXAMS model are used in MEXAMS, the user should be familiar with the calculations made by the model and its data requirements.

SECTION 2

CONCLUSIONS

MINTEQ, a thermodynamic equilibrium geochemical model, has been linked with EXAMS, a steady-state aquatic exposure assessment model, to produce MEXAMS, the Metals Exposure Analysis Modeling System. As a result, much of the complex chemistry affecting the behavior of selected priority pollutants in aquatic systems can be explicitly considered. Specifically, chemical speciation and its effect on the adsorption and precipitation of metals can be considered. MEXAMS should, therefore, provide more accurate predictions of the metal concentrations likely to be found in different aquatic systems. It should also overcome some of the limitations inherent in earlier attempts to model the behavior of metals.

MEXAMS is applicable to a fairly broad range of problems associated with the impacts of priority pollutant metals on aquatic systems. It can be used to perform both screening level and site specific analyses of different sources of metals such as industrial discharges and mine drainage. It can also be used to support the interpretation of data collected during aquatic bioassays and as a framework for guiding future research.

The modeling system contains an interactive program that helps the user prepare water quality data for input to MINTEQ. It also queries the user to obtain user run information which is then used to control the operation of

MINTEQ and EXAMS and the transfer of simulation results back-and-forth between the models. Thus, the effort required to use the system is minimized.

SECTION 3

RECOMMENDATIONS

The Metals Exposure Analysis Modeling System, MEXAMS, should be applied to a series of aquatic systems to: 1) demonstrate the importance of explicitly considering the effects of precipitation, adsorption and aqueous speciation when assessing the behavior of metals in aquatic systems, and 2) identify any limitations that could impact the applicability of the modeling system. Initial applications should be made to hypothetical, but representative, aquatic systems to identify important processes and critical data needs. This should be followed by applications to one or more site specific problems.

Available thermodynamic data for antimony, berylium, chromium, mercury, selenium and thallium should be reviewed for entry into the MINTEQ thermodynamic data base. Clearly, this effort should take advantage of the review work that has already been performed by other geochemical modelers. This would broaden the applicability of MEXAMS to all of the priority pollutant metals contained in the EPA/NRDC Settlement Agreement (as modified).

The literature should be reviewed to obtain available thermodynamic equilibrium constants and other accessary data for the formation of organic complexes. This effort would overcome one of the major limitations of the modeling system.

Attention should be given to the development of efficient techniques for coupling geochemical models with more complex aquatic transport models. This would provide the capability to conduct detailed, site-specific waste-load allocation studies, particularly for those aquatic systems where water quality variations and/or the movement of water and sediments are highly dynamic.

In conjuction with the development of such techniques, research should be initiated to develop approaches for handling the kinetics of precipitation/dissolution, adsorption/desorption and oxidation/reduction. In the first two cases, this research should largely focus on the review of existing data and experimental work directed at filling critical data gaps. In the latter area, research should be focussed on developing both a better understanding of oxidation/reduction mechanisms and appropriate algorithms for inclusion in geochemical models.

SECTION 4

DESCRIPTION OF MEXAMS

This section provides a brief introduction to MEXAMS. It overviews each of the components in MEXAMS and the operation of the overall modeling system. It also describes the types of analyses that can be performed with MEXAMS and the limitations the user should be aware of before using the system.

MEXAMS COMPONENTS

MEXAMS consists of three components: 1) a geochemical model, 2) an aquatic exposure assessment model, and 3) a user interactive program. The geochemical model simulates the complex chemical interactions that affect metal behavior in natural waters. The exposure assessment model simulates the transport processes affecting metal migration and fate in aquatic systems. The user interactive program links the two models and aids in the application of the overall system. Figure 1 shows how these three components are linked. Each component is discussed in more detail below.

MINTEQ is the geochemical model in MEXAMS. It is a thermodynamic equilibrium model that computes aqueous speciation, adsorption and precipitation/dissolution of solids. Speciation is calculated using an

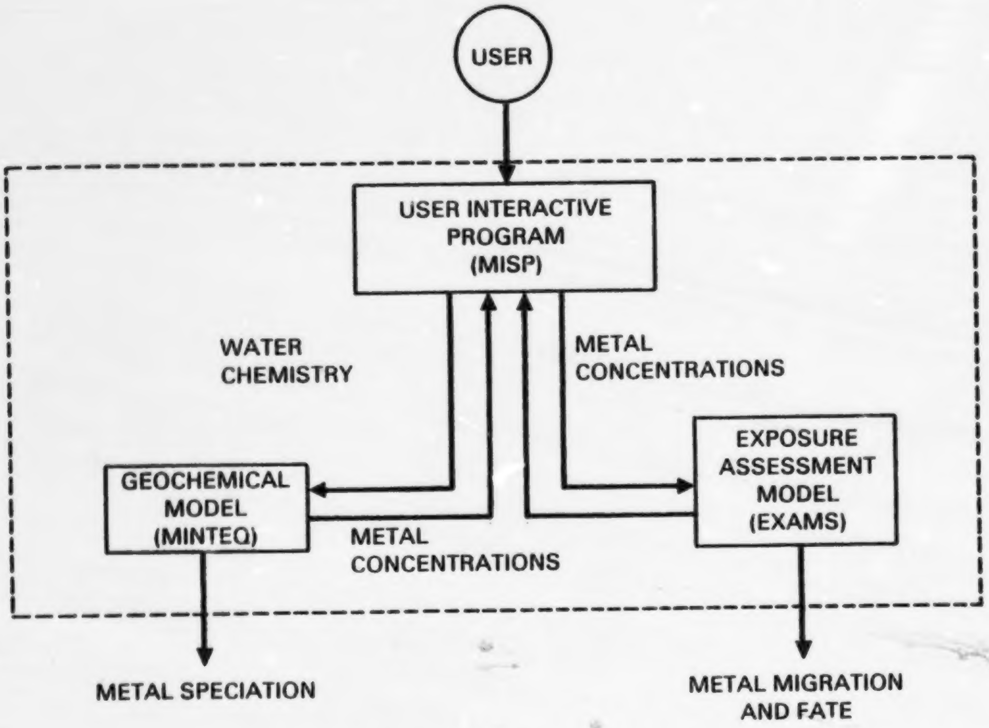

USER
USER INTERACTIVE PROGRAM (MISP)
WATER CHEMISTRY
METAL CONCENTRATIONS
GEOCHEMICAL MODEL (MINTEQ)
EXPOSURE ASSESSMENT MODEL (EXAMS)
METAL CONCENTRATIONS
METAL SPECIATION
METAL MIGRATION AND FATE

Figure 1. Schematic showing overall structure of MEXAMS

equilibrium constant approach wherein a series of mass action expressions are solved subject to mass balance constraints on each chemical component. A knowledge of how a metal will speciate is important for two reasons. First, in order to accurately predict how much metal will be taken out of solution by precipitation and adsorption, the aqueous speciation must be known. Second, since the toxicity and bioavailability of individual species can vary by several orders of magnitude, a knowledge of metal speciation is needed to make accurate estimates of aquatic impacts.

In MINTEQ, adsorption is treated as being analogous to aqueous speciation. As a result, mass action expressions can be formulated for adsorption reactions. MINTEQ contains six algorithms for calculating adsorption. The first is a single valued partitioning coefficient or Kd that has been corrected for the activity of the metal species binding to the surface. The corrected value is called an "activity Kd", and since it is independent of the aqueous speciation, it may be applicable over a broader range of water quality conditions than a standard Kd which is based on concentration. The second algorithm is an "activity" Langmuir isotherm where the Langmuir constants are formulated in terms of the activity of the metal species binding to the surface. The third algorithm is an "activity" corrected Freundlich isotherm where again the Freundlich equation is formulated in terms of the activity of the metal species binding to the surface.(a) The fourth algorithm is for simple ion exchange reactions where the activity ratio of the exchanging species is assumed to remain constant. The constant capacitance model and triple layer model are the other two options. They are more theoretically based approaches that consider the electrostatic potential at the surface of the sorbing media and the effect of pH and ionic strength changes on surface properties.

MINTEQ can compute the mass of metal transferred into or out of solution as a result of the dissolution or precipitation of solid phases. While this calculation is limited by the fact that it is made for equilibrium conditions and precipitation/dissolution reactions may be kinetically controlled, it is possible to obtain reasonable results if the solids considered by MINTEQ as possible equilibrium phases are properly selected. That is, the user must permit MINTEQ to consider only those solids whose formation is not limited by kinetic barriers.

(a) This option is not available on the PDP 11/70 version of MINTEQ.

As with any geochemical model, MINTEQ requires two types of data: 1) thermodynamic data and 2) water quality data. The thermodynamic data are equilibrium constants, enthalpies of reaction and other basic information required to predict the formation of each species or solid phase. The water quality data are the physical and chemical properties of the water body being analyzed. The user only has to generate the water quality data in order to use MINTEQ. The thermodynamic data are contained in a data base that accompanies the model. This data base is constantly being updated and expanded as new or improved data become available.

MINTEQ was developed by combining the best features of two other existing geochemical models: MINEQL (Westall et al. 1976) and WATEQ3 (Ball et al. 1981). MINTEQ uses MINEQL's computational structure. The WATEQ3 features added to the computational structure were the thermodynamic data base and algorithms for correcting changes in water temperature and ionic strength. The overall model is discussed in detail in MINTEQ - A Computer Program for Calculating Aqueous Geochemical Equilibria by A. R. Felmy, D. C. Girvin and E. A. Jenne (1983).

MINEQL was developed to solve a similar class of problems as earlier computer programs such as REDEQL (Morel and Morgan, 1972) and REDEQL2 (McDuff and Morel, 1973) but with a mathematically more general computational method. However, familiarity with the use of these earlier programs will be beneficial when learning to use MINTEQ.

EXAMS, the Exposure Analysis Modeling System, developed by the EPA Environmental Research Laboratory in Athens, Georgia, is the aquatic exposure assessment model in MEXAMS.(a) It is a steady-state model for screening-level exposure assessments that is applicable to rivers and lakes. The model was developed primarily for use with organic compounds, and it provides estimates of exposure, persistence and fate. Operationally, exposure is defined as the pollutant concentrations that would be achieved under steady-state conditions. That is, the resultant concentrations when loadings to the aquatic system are balanced by losses of pollutant from the system as a result of transport and transformation processes. Persistence is defined as the time required for pollutant concentrations to dissipate assuming the pollutant loadings are terminated. Fate is defined as the steady-state distribution of the pollutant within each compartment. The Fate calculation gives the user an indication of the relative importance of each transport and transformation process.

The processes considered by the original EXAMS can be divided into four categories: 1) ionization and sorption, 2) transformation, 3) transport, and 4) chemical loadings. For ionization and sorption, EXAMS can consider up to 15 molecular species of a given pollutant. These include the uncharged parent molecule and its singly- and doubly-charged cations and anions. Each of these can occur in a dissolved, sediment-sorbed or biosorbed form. Equilibrium sorption is calculated using equilibrium distribution coefficients. The second category, transformation processes, includes photolysis, hydrolysis, biolysis and oxidation. Rates of transformation for each process can be assigned to each of the 15 molecular species. The third category, transport processes, includes the movement of dissolved, sediment-sorbed, and biosorbed fractions and volatilization. Since EXAMS does not explicitly compute water and sediment movement, they must be obtained from field measurements or other models. Volatilization is calculated using the two-resistance or "two-film" model. The final category, chemical loadings, includes external pollutant loadings from point sources, non-point sources, dry fallout or aerial drift, atmospheric washout and ground-water seepage. The user's manual and system documentation report for EXAMS provides extended discussions of how each of the above processes are modeled.

(a) Burns, L. A., D. M. Cline and R. R. Lassiter. Exposure Analysis Modeling System (EXAMS): User Manual and System Documentation. U.S. Environmental Protection Agency, Athens, Georgia. EPA-600/3-82-023.

The coupling of EXAMS with MINTEQ required several modifications to the code and the way it is used. Code modifications were designed in such a way that all of the original EXAMS options and capabilities were retained, and no additional input data would be required. Most of the modifications related to by-passing unnecessary calculations or calculations either not applicable to metals or duplicated by MINTEQ. For instance, there is no need for EXAMS to compute adsorption since MINTEQ will provide the quantity of metal sorbed to sediments and biota. Modifications of this type were handled largely without changing the code. Another example is chemical degradation which is applicable to organics but not to metals. Through the proper specification of EXAMS inputs, most of these calculations can be by-passed. This means that the user does not have to maintain two different versions of EXAMS, one for organics and one for metals. The other modifications related to the expansion of the EXAMS algorithms to consider the precipitated fraction of the metal. This involved modifying the transport algorithm. It also involved adding a scheme to by-pass the solubility limitation of 50% of the aqueous solubility or 1 x 10^{-5} M for the neutral species if the model is being used for metals. Section 6 of this report contains a detailed discussion of the specific modifications made to EXAMS.

MISP, the MEXAMS Interactive Software Program, is the third component in MEXAMS. It has several important functions. First, it helps the user input data to MINTEQ. Input data for EXAMS are not handled by MISP; they must be prepared using the procedure outlined in the EXAMS User's Manual. However, the program does access the EXAMS input file once it has been prepared. MISP also queries the user to obtain more specific information on whether MINTEQ will be used alone or in combination with EXAMS, and the types of output information the user would like. Finally, and most importantly, MISP links MINTEQ with EXAMS and controls the operation of each model. This linkage consists of a series of event flags that are passed back and forth between the models that tell EXAMS or MINTEQ when to start or stop execution and which data files to access.

OPERATION OF MEXAMS

MEXAMS can be operated in three modes: 1) the MINTEQ-only mode, 2) the EXAMS-only mode, and 3) the coupled MINTEQ and EXAMS mode. The MINTEQ only mode allows the user to analyze how changes in water chemistry will affect the behavior of a metal without regard for the effect of transport processes. The EXAMS only mode functions exactly like the original EXAMS model. The coupled MINTEQ and EXAMS mode allows the user to also consider the effect of transport processes and chemical interactions.

The operation of MEXAMS in the MINTEQ-only mode is very straightforward. The user simply enters MISP and selects this mode. If a MINTEQ input file is not already available, the user is queried for information on the physical and chemical characteristics of the water being analyzed. This information is used to construct an input data file for MINTEQ. The user can create any number of files using this procedure. Once they are created, the user can initiate MINTEQ and wait for the results. MINTEQ input files can only be created in the MINTEQ-only mode.

The EXAMS-only mode only requires an EXAMS input file. MISP will copy this file to the EXAMS input file FOR005.DAT.

In the coupled mode the operation is more complex. Before entering MISP, the user must create an EXAMS input file that describes the characteristics of the aquatic system and metal loadings being assessed. This is not a difficult process. It involves following the instructions given in Section 6 of this report and the EXAMS user's manual. The user then enters MISP and selects the coupled mode. This procedure is the same as that for the MINTEQ only mode, MISP will query the user for a MINTEQ input file for each EXAMS compartment or set of compartments with different water quality characteristics. The MINTEQ input files can be created by previous runs of MISP in the MINTEQ only mode or by following the precedure outlined in Appendix C for preparing MINTEQ input files. The user will be queried to provide some run-specific information that controls the number of times metal concentrations are updated by MINTEQ. MEXAMS is now ready to simulate metal behavior, migration and fate.

The first step in the calculation is for EXAMS to make an initial exposure calculation assuming no adsorption or precipitation. This calculation provides an initial distribution of dissolved metal concentrations in each compartment of the aquatic system. These concentrations, along with the suspended sediment and biota concentrations for each compartment, are then transferred to MISP. MISP passes the dissolved metal concentration in the first compartment to MINTEQ along with a flag telling MINTEQ to read the water quality data for that compartment. MINTEQ uses these data to obtain an improved estimate of the concentrations of metal in solution, adsorbed to sediments, adsorbed to biota and in a precipitated form for the compartment. These results are passed back to MISP where they are summed and divided by the total to obtain metal fractions (e.g., the fraction of the metal in solution, adsorbed or precipitated). MISP then proceeds to the second compartment. If the water quality conditions of this compartment are identical to the first and the total metal concentrations are approximately the same (within 5% of each other), then MISP simply uses the same fractions calculated for the first compartment and MINTEQ is not called. If the total metal concentrations differ by more than 5%, another MINTEQ calculation is performed. This calculation is faster because MINTEQ has already read the water quality data and has stored the results of the previous calculation. An entire new calculation is made only when MISP encounters a compartment with completely different water quality conditions.

Once all of the metal fractions have been computed, MISP passes them back to EXAMS for insertion in its ALPHA array. This array is used throughout EXAMS to compute pollutant transformation and transport. At this point, EXAMS again predicts exposure levels (i.e., new dissolved, adsorbed and precipitated metal concentrations in each compartment). The option now exists for EXAMS to iterate again with MINTEQ or proceed to calculate fate and persistence. This decision depends on the number of iterations specified by the user before initiating the simulation.

Upon completion of the exposure calculation, EXAMS sums the flux rate of pollutant attributable to each transport and transformation process over the entire aquatic system, and then computes the significance of each process by dividing each flux rate by the total of the external loadings. This gives a percentage for each flux rate that is reported as an analysis of metal fate.

The persistence calculation in EXAMS involves terminating the chemical loadings and computing the dissipation of the chemical over approximately two system-level halflives. To limit the number of computations, the estimated time frame required to achieve two halflives is divided into 12 equal increments of time. Since metal concentrations in each compartment will probably change throughout the persistence calculation, periodic updates of the metal fractions in the ALPHA matrix may be required. Therefore, the user is given the option to have the metal fractions updated after every persistence calculation, every other calculation, every third calculation, every fourth calculation, every fifth calculation or not at all. The number of times is specified by the user before initiating the simulation.

Outputs from EXAMS, MINTEQ, and MISP are provided after the completion of the persistence calculation. The EXAMS outputs give exposure, fate and persistence predictions. The MINTEQ outputs give details on the chemical interactions occurring in each compartment. The MISP output gives a brief summary of the EXAMS-MINTEQ interactions. The EXAMS,MINTEQ and MISP outputs are in files FOR002.DAT, MINTEQ.OUT and MISP.OUT, respectively.

APPLICABILITY

MEXAMS, as it was originally conceived, was developed to provide EPA with a predictive tool capable of performing screening level analyses. The user can create a series of MINTEQ input files describing a broad range of water quality conditions in order to evaluate how a specific priority pollutant metal will speciate, adsorb or precipitate. Using the many generalized environments that have been created for EXAMS, or any other type of general aquatic environment, the user can also rapidly evaluate exposure, fate and persistence. This type of application would give the user some indication of which processes are of importance in different types of aquatic systems and which types of systems are most likely to be impacted by metals.

MEXAMS can also be used on a more site-specific basis to investigate the potential impacts of different metal sources like industrial discharges or mine drainage. Such applications can include the use of MINTEQ alone or in conjunction with EXAMS. An example of the former is a study by Morel et al. (1975) on the fate of trace metals discharged from a Los Angeles County treatment plant. They used a geochemical model to show how the oxidation and dilution of sewage by seawater would affect the fate of different metals. An example of the latter are the recently published studies by Chapman et al. (1982) and Chapman (1982) on the impacts of mine drainage on the quality of a creek in Australia.

Another application of MEXAMS relates to improving the information available from bioassays. Historically, only the "total" concentration of metal present was measured during the performance of aquatic bioassays. This is largely the reason the current Federal criteria are based on "total recoverable" levels. If the chemistry of the dilution waters were known, MEXAMS, more specifically MINTEQ, could be used to estimate the dissolved concentration of metal present during the bioassay, as well as the species that were present. The former would provide a means of adjusting the current standards to a dissolved metal basis. This would provide more reasonable standards since the dissolved fraction is likely to be the most toxic and bioavailable. Estimates of the concentration of aqueous species of metal present during the bioassays would begin to provide a basis for setting standards based on the toxic species. This is essentially the procedure Andrew et al. (1977), Chakoumakos et al. (1979) and Allen et al. (1980) used to identify the toxic metal species in their bioassays. While it is realized that the key information required to do this, namely the chemistry of the dilution waters, may not be available for most of the past bioassays, the use of a geochemical model like MINTEQ during the performance of future bioassays should be considered so that an improved toxicity data base can be developed.

The final application is a more subtle, but equally important, one. It involves the use of MEXAMS as a framework for identifying what is and what is not known about the behavior of priority pollutant metals in aquatic systems. One of the overriding philosophies in developing MEXAMS was to produce a tool that is not only applicable with existing data sources, but also one that helps guide the collection of data in the future. An example of this is the range of options available for calculating adsorption in MINTEQ. The activity Kd, activity Langmuir or Freundlich options can be used given existing data in the literature. The use of the constant capacitance or triple layer models, however, may require the collection of new data. As these data become available, our ability to predict the effects of adsorption will improve. Thus, the model (i.e., MINTEQ) will help identify the critically important data, and guide future research and the collection of better data.

LIMITATIONS

Despite the many capabilities that both MINTEQ and EXAMS offer, there are several limitations that the user must be aware of prior to applying MEXAMS. First, the thermodynamic data base associated with MINTEQ only contains equilibrium constants and accessary data for the following priority pollutant metals: As, Cd, Cu, Pb, Ni, Ag and Zn. Some data on the other metals (i.e., Sb, Be, Cr, Hg, Se and Th) exist in the literature. However, before they can be included in the data base, the data should be carefully evaluated. One of the key areas in geochemical modeling is the quality of the thermodynamic data bases associated with different models. Considerable resources and care have gone into the construction of the MINTEQ data base. It is continually being updated as new and better data are found in the literature. Data for other constituents, some of them priority pollutant metals, are being included under related research programs. At this time, however, the user can only analyze the above metals, unless of course the user has access to or has collected other thermodynamic data.

The second limitation relates to organic complexation. In many natural waters this phenomena can have a major impact on the speciation of metals. While MINTEQ is computationally capable of considering organic complexation, the thermodynamic data base does not contain the necessary equilibrium constants and accessary data. Again, the literature does contain some thermodynamic data on organic complexation of selected metals. These data need to be reviewed and evaluated before inclusion. MISP can be used to enter these data, if they are available to the user.

Another limitation of MINTEQ, and most other geochemical models, is that it treats precipitation/dissolution, oxidation/reduction and adsorption as equilibrium processes, when in fact they may not be in equilibrium. In the area of precipitation/dissolution, some literature data are available on the rates of formation and dissolution of selected solids. However, these data are relatively scarce. Thus, there is a need to experimentally measure the rates of formation and dissolution for those solids that are likely to control metal solubilities in natural waters. There is also a need to include these data in the data base and incorporate a kinetic algorithm in MINTEQ. The kinetics of oxidation/reduction reactions are not well understood. Redox reactions are frequently biologically mediated and rarely in equilibrium. As a result, the equilibrium approach used in most geochemical models can only provide boundary conditions towards which a system is proceeding. It is not clear how important the kinetics of adsorption are for metals. Most constituents tend to adsorb quite rapidly (i.e., within hours), but desorb less rapidly. As in the case of precipitation/dissolution kinetics, there are some data available on the kinetics of adsorption for selected metals. These data need to be included in the data base and supplemented with experimental work.

A final limitation is the degree of testing MEXAMS has received. While both MINTEQ and EXAMS have been tested on and applied to a number of problems, the linked system of models has received limited testing. MEXAMS has only been tested using the relatively simple problems that are described later in this manual. For this reason, users should exercise extreme care in the early stages of applying MEXAMS. Eventually, MEXAMS should be more rigorously tested on a series of hypothetical and site-specific problems.

SECTION 5

A PRIMER ON KEY CONCEPTS IN AQUEOUS CHEMISTRY

It is necessary to first introduce some elementary chemical concepts in order to understand, use and interpret the results obtained from MEXAMS. This section provides an introduction to aqueous speciation, activity, adsorption, and solid phase reactions.

AQUEOUS SPECIATION

The total dissolved fraction of a metal consists of several aqueous species. As an example the possible dissolved species of lead in a water containing nitrate, chloride, sulfate, fluoride and carbonate are shown in Table 1. The total dissolved concentration of lead is then the sum of the concentration of all aqueous species of lead. Equation (1) gives a mass balance for lead.

$$Pb_{\text{total,dissolved}} = m\ Pb^{2+} + m\ Pb(OH)_2(AQ) + m\ Pb(OH)_3^- + 2m\ Pb_2\ OH^{3+} \ldots (1)$$

where

m = molality.

TABLE 1. DISSOLVED SPECIES OF PB

Pb^{2+}

$Pb(OH)_2$ (AQ)

$Pb(OH)^-{}_3$

$Pb_2(OH)^{3+}$

$Pb_3(OH)_4^{2+}$

$PbNO^+{}_3$

$PbSO_4$(AQ)

$Pb(CO_3)_2^{2-}$

$PbCl^+$

$PbCl_2$ (AQ)

$PbCl_3{}^-$

$PbCl_4^{2-}$

$PbF_3{}^-$

PbF^+

PbF_2(AQ)

PbF_4^{2-}

The quantity of each individual species in Equation (1) can be calculated using mass action expressions. Ignoring the difference between the thermodynamic activity and concentration, the formation reactions for the species $PbOH^+$ and $PbCl^{2+}$ are

$$Pb^{2+} + H_2O \rightleftarrows PbOH^+ + H^+ , \quad K_{PbOH^+} \tag{2}$$

$$Pb^{2+} + Cl^- \rightleftarrows PbCl^+ , \quad K_{PbCl^+} \cdot \tag{3}$$

Equations (2) and (3) may be rewritten to yield the mass action expressions,

$$\frac{[PbOH^+]\,[H^+]}{[Pb^{2+}]\,[H_2O]} = K_{PbOH^+} \tag{4}$$

$$\frac{[PbCl^+]}{[Pb^{2+}]\,[Cl^-]} = K_{PbCl^+} \tag{5}$$

where brackets indicate concentrations.

The formation reactions for the species in Table 1 can be conveniently expressed in terms of $[Pb^{2+}]$, $[H^+]$, $[H_2O]$, $[Cl^-]$, $[SO_4^{2-}]$, $[F^-]$, $[NO_3^-]$, $[CO_3^{2-}]$ as well as the equilibrium constants (K) for each species. An important point to note is that the concentration of species which comprise the total dissolved lead in solution depends upon $[H^+]$, $[Cl^-]$, $[SO_4^{2-}]$, $[F^-]$, $[NO_3^-]$ and $[CO_3^{2-}]$. In the example, if these constituents (i.e., pH, chloride, sulfate, fluoride, nitrate and carbonate) are not determined in a water analysis, an inaccurate aqueous speciation calculation could result.

Redox reactions are also related to the mass balance equations and mass action expressions in a similar manner to those just presented. Table 2 presents the aqueous species of iron in a solution containing only chloride, phosphate and sulfate. Since, in an aqueous solution, iron can exist in two oxidation states, two mass balance equations can be written, one for each oxidation state.

$$Fe(II)_{total,\ dissolved} = m\ Fe^{+2} + m\ FeOH^+ . . . . \tag{6}$$

$$Fe(III)_{total,\ dissolved} = m\ Fe^{+3} + m\ FeOH^{2+} . . . \tag{7}$$

In this notation Fe(II) will represent the total dissolved iron in oxidation state (II) and Fe^{2+} will represent only the concentration of the individual species Fe^{2+}. All of the species of Fe(II) can be written in

TABLE 2. AQUEOUS SPECIES OF IRON

Fe(II)	Fe(III)	
Fe^{2+}	Fe^{3+}	$FeHPO_4^+$
$FeOH^+$	$FeOH^{2+}$	$FeH_2PO_4^{2+}$
$Fe(OH)_3^-$	$Fe(OH)_2^+$	FeF^{2+}
$Fe(OH)_2(AQ)$	$Fe(OH)_3(AQ)$	FeF_2^+
$FeH_2PO_4^+$	$Fe(OH)_4^-$	$FeF_3(AQ)$
$FeHPO_4(AQ)$	$Fe_2(OH)_2^{4+}$	$FeSO_4^+$
$FeSO_4(AQ)$	$Fe_3(OH)_4^{5+}$	$Fe(SO_4)_2^-$
	$FeCl^{2+}$	
	$FeCl_2^+$	
	$FeCl_3(AQ)$	

terms of Fe^{2+} and all species of Fe(III) can be written in terms of Fe^{3+} using mass action expressions. The two oxidation states are then linked by the redox reaction for Fe^{2+} and Fe^{3+}.

$$Fe^{3+} + e^- \rightleftarrows Fe^{2+}, \tag{8}$$

resulting in the mass action expression,

$$\frac{[Fe^{2+}]}{[Fe^{3+}]\,[e^-]} = K_{Fe^{2+},Fe^{3+}} \quad . \tag{9}$$

Equation (8) is written between the species Fe^{2+} and Fe^{3+} and not between the total concentrations of Fe(II) and Fe(III). The use of Equation (9) and knowledge of the Eh or pE will allow total dissolved iron to be correctly partitioned into the species shown in Table 2.

ACTIVITY

The concentration of a species is related to the thermodynamic activity by the activity coefficient.

$$[Pb^{2+}]\,\gamma_{Pb^{2+}} = \{Pb^{2+}\} \quad . \tag{10}$$

where brackets denote concentration, γ is the activity coefficient and { } denotes activity. The difference between activity and concentration can be thought of as analogous to the difference between ideal and real gases. The activity coefficient takes into consideration interactions between charged ions and ion interaction with the bulk solution. The activity coefficient varies with: species charge, species size, temperature and ionic strength (I);

$$I = \frac{1}{2} \sum_{i=1}^{n} m_i \, Z_i^2 \tag{11}$$

where

m_i = concentration of species i

Z_i = charge of species i

n = total number of species in solution.

Since charge, ion size and temperature are usually fixed the most important variable in activity coefficient calculations is usually ionic strength. In very dilute solutions where the ionic strength is approximately zero the activity coefficient is approximately one and concentration equals activity. However, as ionic strength increases the activity coefficient can become very small and the concentration can be as much as two orders of magnitude larger than the actual activity. Since the activity is the true thermodynamic value all of the equilibrium constants, which have been previously described, are only valid when expressed in terms of activities rather than concentrations. As a result, the determination of the ionic strength is important in determining activity coefficients, the resulting activities and the overall modeling results.

ADSORPTION

Adsorption can be thought of as analogous to aqueous speciation since the solid phase has surface adsorption sites which react with solution species. Equation (12) is a mass action expression for lead adsorption.

$$\overline{SO} + Pb^{2+} \rightleftarrows \overline{SOPb}^{+} \quad \text{and} \quad \overline{K_{SOPb}}^{+} = \frac{\{\overline{SOPb^{+}}\}}{\{SO^{-}\}\ \{Pb^{2+}\}} \qquad (12)$$

where $\overline{SO}^{-}$ represents a surface site, $\overline{SOPb}^{+}$ represents a surface bound Pb^{2+} ion and $\overline{K_{SOPb}}^{+}$ represents the equilibrium constant for the reaction.

The mass balance for lead can now be rewritten to include adsorbed species, Equation (13).

$$Pb_{total} = mPb^{2+} + m\ PbOH^{+} \ldots + m\ \overline{SOPb^{+}} \quad . \qquad (13)$$

Equation (13) is now written in terms of dissolved plus adsorbed lead rather than total dissolved lead, Equation (1). The total adsorbed and dissolved lead does not include lead precipitates, such as $PbCO_3(s)$. Formulating adsorption reactions in an analogous manner to aqueous speciation reactions also introduces a mass balance equation for available adsorption surface sites (Equation 14).

$$\overline{SO}_{total} = \overline{SO^{-}} + \overline{SOH} + \overline{SOH_2^{+}} \ldots \overline{SOPb^{+}} \quad . \qquad (14)$$

Unfortunately, this simple concept of adsorption ignores an important difference between adsorption onto solid phases and aqueous speciation, i.e., the general presence of an electrical charge on the solid surface. This charge creates an electrostatic potential between the surface and bulk solution. The charge and electrostatic potential can markedly effect adsorption and alter the simplistic concept presented here. Section 4 of the MINTEQ technical document discusses this further.

SOLID PHASE REACTIONS

A solid phase can also be represented by a formation reaction and mass action expression, e.g.,

$$Pb^{2+} + CO_3^{2-} \rightleftarrows PbCO_3(s), \text{ and} \qquad (15)$$

$$\frac{\{PbCO_3(s)\}}{\{Pb^{2+}\}\ \{CO_3^{2-}\}} = K_{PbCO_3(s)} \qquad (16)$$

where {} denotes activity.

If the pure solid phase is present, then the activity of $PbCO_3(s)$ is unity. This leads to the concept of a saturation index for a solid phase. The concept of a saturation index is easier to understand if the reaction for the solid is written as a dissolution reaction, Equation (17).

$$PbCO_{3(s)} \rightleftarrows Pb^{2+} + CO_3^{2-} \qquad (17)$$

with the mass action expression,

$$\frac{\{Pb^{2}\}\ \{CO_3^{2-}\}}{\{PbCO_3(s)\}} = K_{PbCO_3(s)} \qquad (18)$$

A simple rearrangement of Equation (18) and taking logarithms yields Equation (19).

$$\log SI = \log AP/K \qquad (19)$$

where

AP = activity product ($\{Pb^{2+}\}\ \{CO_3^{2-}\}$), and SI = saturation index.

At equilibrium log SI will of course equal zero, Equation (19). If the solid phase is undersaturated, then log K > log AP and log SI is negative. If the solid phase is supersaturated, then log K < log AP and log SI is positive.

The saturation index is a very useful indicator of the tendency of a solid to dissolve or precipitate or of how close the solid is to equilibrium. However, it does not mean the solid will actually dissolve or precipitate. Kinetic factors may prevent the solid from ever actually attaining equilibrium in the time frames of interest. Therefore, when using a geochemical model it will be very important to carefully choose which solids will be allowed to dissolve or precipitate. Allowing the model to dissolve or precipitate solids that will not reach equilibrium in the time frames of interest can lead to erroneous results. Some general guidelines for selecting solid phases will be presented in Section 6.

SECTION 6

GUIDELINES FOR USE

Section 6 presents the user with detailed guidelines for the use of MEXAMS. It starts by presenting the modifications made to the EXAMS model in order to link it with MINTEQ, as well as data input procedures which supplement those provided in the EXAMS user's manual. Next, it discusses the user options and general data requirements for MINTEQ. This is followed by step-by-step procedures for entering data into MEXAMS using MISP. The section concludes by outlining the types of output available from MEXAMS and typical responses to error messages.

USE OF EXAMS

The use of EXAMS is covered in detail in the EXAMS user's manual and documentation report.(a) This discussion will not attempt to duplicate what is already provided in this report. Rather, it will focus on the modifications that were made to EXAMS in order to link it with MINTEQ. All of the modifications discussed below are for the batch version of EXAMS. The specific coding changes made to each subroutine in EXAMS are discussed later in Section 7, the Programmer's Supplement.

(a) Burns, L. A., D. M. Cline and R. R. Lassiter. Exposure Analysis Modeling System (EXAMS): User Manual and System Documentation. U.S. Environmental Protection Agency, Athens, Georgia. EPA-600/3-82-023.

EXAMS Modifications

Modifications to EXAMS are transparent to the user familiar with the original code. All changes are internal and do not affect computations performed without the geochemical code coupling: the capability of the modified version of EXAMS is exactly the same as the unmodified version. Basically two types of modifications were made to the EXAMS model. The first type involved by-passing those calculations that were unnecessary for heavy metal ions or duplicated by MINTEQ. The second type involved additions to account for the migration and fate of the precipitated fraction. Specific modifications included:

1. Since MINTEQ computes the concentration of dissolved species present in each compartment, there is no need to consider ionization in EXAMS. In reviewing the code it was found that the ionization computations could be by-passed through the proper selection of model inputs.

2. Since MINTEQ computes the quantities of metal sorbed to sediments and biota for each compartment, there is no need for EXAMS to make this calculation. Again it was found that this modification could be handled through the proper selection of inputs, as opposed to the modification of the code. Supplemental input procedures for this modification are also discussed later.

3. The unmodified version of EXAMS limits the solubility of a chemical to either less than 50% of its aqueous solubility or 1×10^{-5} M for the dissolved neutral form of the chemical. Thus, it does not allow for precipitation. In the modified version of EXAMS, these limitations are by-passed. In addition, the bookkeeping algorithm in EXAMS which keeps track of the quantities and forms of chemical present in each compartment was expanded to include the precipitated fraction. This involved expanding the ALPHA matrix so that ALPHA(16) is now the precipitated fraction. The dissolved, sediment-sorbed and biosorbed fractions are now ALPHA(17), ALPHA(18) and ALPHA(19), respectively, instead of ALPHA(16), ALPHA(17) and ALPHA(18). Wherever these quantities were used in the code they were changed.

4. EXAMS will compute steady-state metal concentrations by solving the following equation:

$$L_e + L_i - VKC = V\frac{dc}{dt} = 0 \qquad (20)$$

where

C = total metal concentration
K = overall pseudo first order loss constant that expresses combined effects of transport and volatilization
L_e = total external loading on the compartment
L_i = total internal loading on the compartment
V = water volume in the compartment.

In order to account for the migration of the precipitated fraction it was assumed that it could be transported as a sediment-sorbed fraction. This did not require any changes be made to the transport equation, but did require modifying the calculation of the internal chemical loading (L_i) for each compartment. L_i is now calculated as follows:

$$L_i = C * [\mathrm{ALPHA}(17) * \mathrm{SUMWAT} + (\mathrm{ALPHA}(16) + \mathrm{ALPHA}(18)) * \frac{\mathrm{SUMSED}}{\mathrm{SEDCON}} + \mathrm{ALPHA}(19) * \mathrm{SUMWAT} * \mathrm{PLRAG}]$$

where

L_i = total internal loading for the ith compartment (mg/hr)

C = total metal concentration (mg/l)

ALPHA(16), ALPHA(17), ALPHA(18), and ALPHA(19) = fractions of precipitated, dissolved, sediment-sorbed and biosorbed metal, respectively;

SUMWAT = total water discharge

SUMSED = total sediment discharge

SEDCON = sediment concentration per unit volume of water

PLRAG = fraction of biomass in a compartment.

5. Dispersion processes for metals in the modified EXAMS are expressed in the same way as in the original EXAMS, except for the dispersion between water and benthic columns. In this case, a portion of the

return "flow" (SEDFL) of suspended sediment from the water compartment to the benthic compartment, due to dispersion, is computed in the modified EXAMS as:

$$\mathrm{SEDFL} = \mathrm{TEMSED} * \frac{\mathrm{ALPHA(17,W)} * \mathrm{SEDCOL(W)}}{\mathrm{ALPHA(16,W)} + \mathrm{ALPHA(18,W)}} * \frac{\mathrm{ALPHA(16,b)} + \mathrm{ALPHA(18,b)}}{\mathrm{ALPHA(17,b)} * \mathrm{SEDCOL(b)}}$$

$$\mathrm{TEMSED} = \mathrm{SEDCOL(W)} * \frac{\mathrm{WATVOL(W)}}{\mathrm{VOLG(W)}} * \frac{\mathrm{DSPG} * \mathrm{XSTURG}}{\mathrm{CHARLG}}$$

where

b,W = values in water and benthic compartments, respectively

CHARLG = characteristic length

DSPG = dispersion coeffient

VOLG = volume of a compartment

WATVOL = water volume

XSTURG = surface area.

6. Metals are largely unaffected by the transformation and degradation processes which govern the fate of organics in natural waters. For this reason, these processes are bypassed in the modified version of EXAMS whenever the metal option is exercised.

Supplemental Input Data Procedures

Since no new input data are required for the modified version of EXAMS, the input data procedures for the original EXAMS can be used. Section 3.4 of the original EXAMS user's manual provides procedures for the preparation of batch input data. One need only select the generic heavy metal as the chemical to be modeled; loadings and environments are input in the original manner.

MINTEQ TUTORIAL

To learn to use MINTEQ, begin with a single hypothetical problem (such as 0.01 molar solution of Na^+ and Cl^-). In this way, the large number of input options will not be overwhelming.

The first step is to learn to prepare MINTEQ input data. There are two methods of preparing MINTEQ input files: 1) the input file can be prepared directly utilizing the file description given in Appendix C, 2) a user interactive routine in MISP can be used to prepare the input files.

Experienced users will find the first option preferable because the user interactive routine in MISP is lengthy. However, beginning users will find the user interactive routine helpful in defining the data needs for MINTEQ.

To use the interactive routine type,

"RUN MISP <CR>",

and select the MINTEQ only mode without EXAMS (Option 2). Answer, 'N', when asked if a data file is ready. Next, a series of questions will appear on the screen. These questions are described in detail in the "DATA INPUT TO MEXAMS USING MISP" section. There are a total of 55 questions in this routine; for this simple hypothetical problem you will want to give the following responses.

Question No. 1: Enter title of simulation

Answer: 0.01 molar NaCl solution

Question No. 2: Enter description of water body.

Answer: hypothetical solution

Question No. 3: Select data units

Answer: select molality (MOL)

Question No. 4: Enter temperature (degree centigrade)

Answer: 25.0

Questions Nos. 5 through 10:

Answer: N

Question No. 11: How many iterations will you allow?

Answer: select 40 (option 0)

Questions Nos. 12 through 13:

Answer: N

Question No. 14: Enter debug option number.

Answer: No debug (option 0)

Questions Nos. 15 through 25:

Answer: N

Question No. 26: Does your sample contain CL?

Answer: Y

Enter total CL>

Answer: 0.01

Do you want to guess the activity of CL?

Answer: N

Questions Nos. 27 through 36:

Answer: N

Question No. 37: Does your sample contain NA?

Answer: Y

Enter total NA>

Answer: 0.01

Do you want to guess the activity of NA?

Answer: N

Questions Nos. 38 through 55:

Answer: N

After you have completed this question/answer session, select the "MODEL DATA" option. When the program has finished, a copy of the output will be in file MINTEQ.OUT.

At this point, the sections "USE OF MINTEQ" and "DATA INPUT TO MEXAMS USING MISP" should be reviewed. Later, the interactive routine can be used to create different MINTEQ input files (select the store data in a file option) and the file structure can be compared with the description given in

Appendix C. In this way, it will be much easier to learn the procedure given in Appendix C and also to gain familiarity with the different species type designations.

An example of using MEXAMS in the MINTEQ-EXAMS mode is given in the MEXAMS implementation test case.

USE OF MINTEQ

MINTEQ offers a number of options which provide a great deal of flexibility in the way the user defines the chemistry of the system being modeled. These options make it possible for the user to apply MINTEQ to a very large and diverse problem set. Thus, while not all of the options discussed below are required to use MINTEQ to evaluate the behavior of metals, it is important that the user be aware of these options when preparing input data files.

Description of Species Types

The chemical species in MINTEQ are assigned one of six different species type designations (Westall et al. 1976). In addition to facilitating mathematical computations, these species type designations provide the user with the ability to solve a broad range of chemical equilibrium problems.

Type I Species - Components--

Components are defined as the chemical species that are chosen to represent each chemical constituent in the water analysis. For example, Zn^{2+} is the component for zinc or Cd^{2+} for cadmium. Choosing charged species as components does not conflict with Gibbs original definition of components, since there are no restrictions that components must be the elemental forms (Westall et al. 1976). One component is designated for each oxidation state for the redox sensitive elements included in the MINTEQ data base. Iron then has two components, Fe^{2+} for iron in oxidation state (II), and Fe^{3+} for iron in oxidation state (III).

A complete list of components in MINTEQ along with their designated I.D. numbers is given in Table 3. The first two digits of the I.D. numbers represents the alphabetic order of the chemical symbol of the element in the periodic table and the third digit is an arbitrary designation. As an example, if the chemical symbols for all elements in the periodic table were put in alphabetical order, Ag (silver) would be second and the ID number would be 020.

The selection of components is somewhat arbitrary with the only restriction being that a component cannot be a combination of two other components. As an example both CO_3^{2-} and HCO_3^- could not be chosen as components for inorganic carbon since HCO_3^- can be formed from CO_3^{2-} and H^+. The only exception to this general rule is for redox sensitive elements since the electron does not actually exist in solution.

Designating a set of components allows the mass action expressions to be written in terms of components, Equation (21).

$$Pb^{2+} + Cl^- \rightleftarrows PbCl^+ \tag{21}$$

The chemical equilibrium problem then reduces to finding the activity of each component that correctly satisfies the mass balance constraints.

TABLE 3. COMPONENTS IN MINTEQ

Component	I.D. Number	Component	I.D. Number
E	001	NH_4^+	490
H_2O	002	NO_2^-	491
Ag^+	020	NO_3^-	492
Al^{3+}	030	Na^+	500
H_3AsO_3	060	Ni^{2+}	540
H_3AsO_4	061	PO_4^{3-}	580
H_3BO_3	090	Pb^{2+}	600
Ba^{2+}	100	Rb^+	680
Br^-	130	HS^-	730
CO_3^{2-}	140	S	731
Fulvate	141	SO_4^{2-}	732
Humate	142	H_4SiO_4	770
Ca^{2+}	150	Sr^{2+}	800
Cd^{2+}	160	U^{3+}	890
Cl^-	180	U^{4+}	891
Cs^+	220	UO_2^+	892
Cu^{1+}	230	UO_2^{2+}	893
Cu^{2+}	231		
Fe^{2+}	280		
Fe^{3+}	281		
H^+	330	Zn^{2+}	950
I^-	380	SOH1	990
K^+	410	SOH2	991
Li^+	440	XPSIO	992
Mg^{2+}	460	XPSIB	993
Mn^{2+}	470	XPSID	994
Mn^{3+}	471	SOHB	995

Type II - Complexes--

All aqueous species which are combinations of two or more components are Type II complexes. Some examples of complexes are shown in Table 4 along with their ID numbers.

The ID numbers for complexes are seven digit numbers with the first three digits representing the ID number of the cationic component and the

TABLE 4. AQUEOUS COMPLEXES

Complex	ID
$PbCO_3(AQ)$	6001401
$PbCl^+$	6002800
$CdHCO_3^+$	1601400
$NiSO_4(AQ)$	5407320

next three digits representing the anionic component. The last digit is an arbitrary designation.

Type III - Fixed Species--

Any species with a fixed activity is a Type III species. It is important to note that solids and gases are also species.

Fixed species are commonly of four types:

- components present at a fixed activity such as the pH or pE,
- solid phases which are present in infinite supply,
- gases present at a fixed partial pressure, and
- redox reactions between two components.

Redox reactions are included here because they represent a fixed activity ratio of the components, Equations (22) and (23),

$$\{\mathrm{Fe}^{3+}\} + \{e^-\} \rightleftarrows \{\mathrm{Fe}^{2+}\} \;,\; K_{\mathrm{Fe}^{3+},\mathrm{Fe}^{2+}} \tag{22}$$

$$\frac{\{\mathrm{Fe}^{2+}\}}{\{\mathrm{Fe}^{3+}\}} = K_{\mathrm{Fe}^{3+},\mathrm{Fe}^{2+}} \{e^-\} \;. \tag{23}$$

Type IV - Precipitated Solids Subject to Complete Dissolution--

Type IV species are identical to Type III solid species except these solids have a finite mass. If during the computations the entire mass of a solid dissolves, then the fixed activity relationship between the components is removed. If, however, during ensuing computations the solid becomes oversaturated, the solid can be precipitated and the fixed activity relationship between the components reestablished.

Type V - Dissolved Solids Subject to Precipitation--

Type V species are solid phases which can precipitate if they become oversaturated. The terminology of "Dissolved Solids" or "Precipitated Solids" can be confusing. Precipitated solids are physically present and have a fixed activity. A dissolved solid is not physically present. The saturation index will be checked to see if the solid should be precipitated. When a Type V solid is actually precipitated by MINTEQ, it becomes a Type IV species.

I.D. numbers for solids are seven digit numbers. The first two digits correspond to the mineral group and roughly follow the mineralogical classification in Dana's system (Dana and Ford 1957) and that described by Robie et al. (1978). The mineral group I.D. numbers are given in Table 5. The next three digits represent the leading cation in the chemical formula and the last two digits are arbitrary designations. Table 6 presents some examples of solid phases and their corresponding I.D. numbers.

Type VI - Species Not Considered--

Type VI species are not considered during equilibrium computations. These species are "considered" only after the equilibrium problem has been solved. As an example, the thermodynamic data for an aqueous complex may be suspect and the user may wish to know the affect on the aqueous speciation if the complex were not considered. In such cases the species can be given a Type VI designation.

TABLE 5. MINERAL GROUP I.D. NUMBERS

00	elements	52	borates
10	sulfides	60	sulfates
20	oxides and hydroxides	70	phosphates
30	multiple oxides	72	arsenates
40	bromides	73	vanadates
41	chlorides	80	orthosilicates
42	fluorides	82	chain silicates
43	iodides	84	framework silicates
50	carbonates	86	sheet silicates
51	nitrates		

TABLE 6. SOLID PHASES AND ID NUMBERS

Solid	I.D.
Aragonite	5015000
Calcite	5015001
BaF_2	4210000
Barite	6010000
Dolomite	5015002
Hematite	3028100

Type Modifications

The default designation for components and aqueous complexes in the MINTEQ data base are Type I and II, respectively. There are no default Type III or IV species. Redox reactions and reactions involving gas phases have default Type VI. The solid phases and minerals can be either default Type V or default Type VI depending upon user input options. The user can override the default type designation by modifying the species type. The default type is determined by the location of the species data in the data files. See the Programmer's Supplement for details.

The following discussion presents some specific examples of how to modify the species type designations and equilibrium constants to solve certain types of problems. The user interactive routine in MISP can perform many of these modifications. However, this routine is lengthy and has limited error recovery ability; it should only be used only to help learn how to prepare MINTEQ input files. The examples presented here will be useful when preparing MINTEQ input files.

Gas at a Fixed Partial Pressure--

To specify a gas at a fixed partial pressure it is necessary to designate the species type for the reaction containing the gas as Type III and for the user to modify the equilibrium constant to reflect the partial pressure of the gas. Equations (24) through (29) presents an example for $CO_2(g)$ at a fixed partial pressure of $10^{-3.5}$ atmospheres.

$$CO_3^{2-} + 2H^+ \rightleftarrows CO_2(g) + H_2O \qquad \log K = 18.16 \tag{24}$$

$$\frac{P_{CO_2}\ \{H_2O\}}{\{CO_3^{2-}\}\ \{H^+\}^2} = K \tag{25}$$

$$\frac{\{H_2O\}}{\{CO_3^{2-}\}\ \{H^+\}^2} = \frac{K}{P_{CO_2}} = K \text{ when } P_{CO_2} = 1.0 \tag{26}$$

$$K' = \frac{K}{P_{CO_2}} \qquad P_{CO_2} \neq 1.0 \tag{27}$$

$$\log K' = \log K - \log P_{CO_2} \tag{28}$$

assuming $P_{CO_2} = 10^{-3.5}$,

$$\log K = 18.16 - (-3.5) = 21.66 \tag{29}$$

The user would give the reaction for $CO_2(g)$ a Type III designation and specify an equilibrium constant of 21.66. This example might represent a surface water in equilibrium with atmospheric carbon dioxide.

Fixed pH--

The activity of a component can also be fixed in a similar manner. To fix the pH at 8.00, designate H^+ (ID 330) as a Type III species and modify the equilibrium constant. Equations (30) through (32) present this example. Equation (30) shows that a component is treated as a species on the right side of the equation and as a component on the left side.

$$H^+_C = H^+_S \text{, } \log K = 0.00 \tag{30}$$

$$\frac{\{H^+\}s}{\{H^+\}_c} = K\text{, since } \{H^+_S\} = 1 \tag{31}$$

$$\{H^+\}_c \cdot K = 1 \tag{32}$$

$$\log K = - \log \{H^+\}_c$$

$$\log K = - (-8.00) = 8.00$$

to fix the pH at 8.00 give H^+ a Type III designation with a new log K of 8.00.

Compute the pE from Fe(II) and Fe(III)--

In the case where direct analytical data for total iron in oxidation states (II) and (III) are available the pE can be computed. This computation may be useful if redox potential measurements are not available or the user wants to see if Fe (II) and Fe (III) are in equilibrium with the measured redox potential. The modification simply involves designating Fe^{2+} and Fe^{3+} as components and entering the appropriate mass totals. Enter the electron as a component (ID = 001) and change the type to Type VI since the electron has no mass in aqueous solution.

Enter an "Activity" Kd

The first requirement for including an "activity" Kd is that the original solution in which the standard Kd was determined must first be modeled by MINTEQ in order to obtain the activity of the ion of interest. To model the solution in MINTEQ merely enter the dissolved equilibrium metal concentration and all experimental water quality data such as the pH and alkalinity. MINTEQ will compute the activity of the uncomplexed ion.

The adsorption reaction can be thought of as a reaction between the uncomplexed ion and the surface,

$$\overline{S} + Cd^{2+} \rightleftarrows \overline{SCd}^{2+} \quad . \qquad (33)$$

Where $\overline{S}$ stands for a surface site and $\overline{SCd}^{2+}$ is surface bound Cd^{2+}. The activity Kd is then:

$$\frac{\overline{SCd}^{2+}}{\{Cd^{2+}\}} = \text{"activity" Kd} \qquad (34)$$

Equation (34) is simply the amount of cadmium adsorbed divided by the activity of the Cd^{2+} species in solution. The problem is now trivial, include SOH1 (a surface site component which represents $\overline{S}$) as a Type III fixed species and inert $\overline{SCd}^{2+}$ as a Type II species. An important point remember when dealing with adsorbed species is that the species ID number must be greater than 9900000 or the mass adsorbed will be incorrectly computed. The ID number allows MINTEQ to differentiate between adsorbed and aqueous species for activity coefficient calculations.

Selection of Adsorption Models

MINTEQ contains six algorithms for calculating adsorption: 1) an "activity" Kd, 2) an ion exchange model, 3) an "activity" Langmuir isotherm, 4) an "activity" Freundlich isotherm,(a) 5) the constant capacitance double layer model and 6) the triple layer site binding model. The selection of which model to use depends upon the site conditions, the desired accuracy of the simulation and the availability of data. The reader is referred to the MINTEQ technical document for details of each model. Only a brief discussion is presented here.

The "activity" Kd should give a reliable estimate of adsorption, as long as the surface chemistry of the solid adsorbent remains relatively constant and the pH and ionic strength remain constant. In other words, as long as the surface properties of the adsorbent remain constant, the "activity" Kd will probably give reliable results. In locations where the pH or ionic strength are variable, the "activity" Kd should not be used.

The ion exchange model will be useful if selectivity coefficients for exchange reactions are available. However, selectivity coefficients will generally be available only for bulk electrolyte ions such as Na^+, K^+ and

---

(a) Available only on the VAX version of MINTEQ

Ca^{2+}. Metal adsorption is probably a result of forming covalent bonds with surface sites and thus can not generally be predicted by an ion exchange model.

The "activity" Langmuir has the advantage over the "activity" Kd in that a mass balance on surface sites is considered. This means that at relatively high metal loadings the "activity" Langmuir will probably give more reliable results than the "activity" Kd as long as the solution pH remains relatively constant. Langmuir isotherm data are available for a number of soils but generally not for stream sediments. To convert regular Langmuir isotherm data to an "activity" Langmuir requires modeling the solutions used in the laboratory study with MINTEQ in order to obtain the activity of the uncomplexed ion or binding species. The isotherm must then be replotted to obtain the "activity" Langmuir K and the total surface sites.

The "activity" Freundlich can be used if the laboratory data do not conform to the "activity" Langmuir.(a) Again to determine the "activity" Freundlich parametrs requires modeling the laboratory solutions with MINTEQ to obtain the activity of the uncomplexed or binding metal ion. Data for conventional Freundlich isotherms are available for many soil types but generally not for stream sediments.(b)

(a) To conform to the "activity" Langmuir model a plot of activity uncomplexed ion/amount sorbed versus activity uncomplexed ion should yield a straight line.

(b) The "activity" Freundlich isotherm is not included in the PDP 11/70 version of MINTEQ.

If data for either the "activity" Langmuir or "activity" Freundlich are available they should be used instead of the "activity" Kd because the isotherms consider the effects on adsorption of variable metal concentrations. However, neither isotherm can theoretically handle changes in surface properties resulting from changes in solution pH, ionic strength or variable solid to solution ratios.

The constant capacitance and triple layer models are based on a theoretical approach and should be superior to the "activity" Kd or "activity" isotherms. These models consider charge-potential relationships at the surface and the changing properties of the surface as a result of changes in pH or ionic strength. However, they also may require specific experimental work to obtain the necessary parameters. For example, to obtain the necessary data for the constant capacitance model at a fixed ionic strength would require as a minimum:

- titration curves of the solid phase at least at one ionic strength and no element of interest (metal) present
- titration curves of the solid in the presence of at least one concentration of the element of interest (metal)
- some estimation of total surface sites and specific surface area

If the user wishes to predict adsorption at different ionic strengths a second titration at a different ionic strength with no metal present would be required.

The constant capacitance and triple layer models have been applied to single oxide systems and mixtures of oxides with considerable success. However, they have only recently been applied to heterogeneous solids such as soils or sediments. Further work should be done but the models should provide more accurate results than the simple "activity Kd" or "activity" isotherms especially in systems where the majority of adsorption sites are on hydrous oxides. For further information on these adsorption models see Section 4 of the MINTEQ technical documentation report.

Biosorption can be considered by using the "activity Kd" model. The biosorption coefficient should be corrected for the activity of the component in solution and computed in the same manner as the "activity" Kd. The only difference is the surface site (SOH) should be assigned an I.D. number of 995. As in EXAMS, this option has been provided so that users can evaluate the relative importance of this mechanism. It has not been tested or evaluated in a theoretical sense.

In summary, MINTEQ is structured to allow the user the flexibility of using as much data as are available. If the system being studied has a relatively constant pH and ionic strength, the metal concentrations are relatively low and only limited adsorption data for that solid or sediment are available, the "activity" Kd provides an adequate approach to model metal adsorption. If, however, metal concentrations can be relatively high and variable due to changes in metal loading then one of the "activity" isotherms, either Freundlich or Langmuir, should be used. However, if the solution pH and ionic strength varies,(a) data for the constant capacitance or triple layer models should be obtained.

(a) pH should not vary by more than ±0.5 to 1.0 unit, ionic strength by ±20% depending upon the system.

Selection of Solid Phases

To introduce this discussion, the difference between "selection of solid phases" and "consideration of solid phases" must be defined. Selection of solid phases determines the solids which are actually going to dissolve or precipitate. These solids will be termed "selected solids" in this section. The "consideration of solids" means the solids which were considered during the selection process. These "considered solids" will only dissolve or precipitate if they are "selected". In terms of the species types, Type III and Type IV are "selected" solids, Type V are "considered" solids.

The user can of course arbitrarily select the solid phases and simply declare them either Type III or Type IV depending upon the specific problem. This is the preferred method when MINTEQ is being used in a research type mode where the user is asking a series of "What if " questions: such as "What would the pH be in equilibrium with calcite ". However, when the user does not know which solids are in equilibrium this approach is not practical.

Generally it is best to allow MINTEQ to select the solids, particularly when the number of solids considered during the selection process (i.e., the number of Type V solids) is specified. MINTEQ will then select and equilibrate the thermodynamically stable solids with the aqueous solution.

The problem with this approach is that the thermodynamically stable solids tend to be highly crystalline and have considerable kinetic barriers to precipitation. If such solids are selected the predicted aqueous phase concentrations can be in error by orders of magnitude. The best technique then is to limit the solids MINTEQ considers to a set of amorphous phases without kinetic barriers to precipitation. This way MINTEQ will select and equilibrate the solution with the stable phases which will actually form. Selecting solids in this manner means that the predicted aqueous concentrations will be maximum concentrations since selection of more stable solids would lower the aqueous concentrations. Table 7 presents a recommended list of Type V solids for the priority pollutant metals in the MINTEQ data base.

Data Requirements

The interpretation of the results predicted by MINTEQ becomes more reliable as the users knowledge of the system increases. In the case of input data, the more data the user has on the water chemistry of the system the more accurate will be the predicted results. This does not mean that the user must have data for all of the components listed in Table 3. Many components do not react with other components or are present in such low concentrations that they do not alter the geochemistry of the particular components being studied. With this in mind, the following discussion will focus on the general importance of each input parameter with the hope that the user can glean some ideas for the specific data requirements of any given system. It must be recognized that no set of guidelines will work for all environmental systems.

pH--

pH is the most important parameter required by MINTEQ. Unless the analytical data are from a well defined laboratory system where the total ionizable H, total H^+ (see the MINTEQ technical document), is known, the pH

TABLE 7. RECOMMENDED LIST OF TYPE V SOLIDS

Copper

I.D. Number	Name
5023100	$CuCO_3$
4223100	CuF_2
4223101	$CuF_2 \cdot 2H_2O$
2023100	$Cu(OH)_2$
4123101	Atacamite
5123100	$Cu_2(OH)_3NO_3$
2023101	Tenorite
7023100	$Cu_3(PO_4)_2$
7023101	$Cu_3(PO_4)_2 \cdot 3H_2O$
6023104	$CuSO_4$
5023101	Malachite
5023102	Azurite

Zinc

I.D. Number	Name
4195000	$ZnCl_2$
5095000	Smithsonite
5095001	$ZnCO_3 \cdot H_2O$
4295000	ZnF_2
2095000	$Zn(OH)_2(A)$
5195000	$Zn(NO_3)_2\ 6H_2O$
7095000	$Zn_3(PO_4)_2 \cdot H_2O$
1095000	$ZnS(A)$
6095004	$ZnSO_4 \cdot H_2O$
6095005	Bianchite
6095006	Goslarite
4095000	$ZnBr_2 \cdot H_2O$
4395000	ZnI_2

Cadmium

I.D. Number	Name
5016000	Otavite
4116000	$CdCl_2$
4116001	$CdCl_2 \cdot H_2O$
4216000	CdF_2
2016001	$Cd(OH)_2(c)$
2016000	$Cd(OH)_2(A)$
7016000	$Cd_3(PO_4)_2$
6016003	$CdSO_4$
4016000	$CdBr_2 \cdot 4H_2O$
4316000	CdI_2

Lead

I.D. Number	Name
4160000	Cotunnite
4260000	PbF_2
6060003	Anglesite
1060001	Galena
2060004	$Pb(OH)_2(c)$
5060000	Cerrusite
60000	$PbBr_2$
4360000	PbI_2
7060005	$PbHPO_4$

Nickel

I.D. Number	Name
5054000	$NiCO_3$
2054000	$Ni(OH)_2$
7054000	$Ni_3(PO_4)_2$
1054001	Millerite
6054001	Retgersite

Silver

I.D. Number	Name
4002000	Bromyrite
4102000	Cerarygrite
5002000	Ag_2CO_3
4202000	$AgF \cdot 4H_2O$
4302000	Iodyrite
7002000	Ag_3PO_440
1002000	Acanthite
6002000	Ag_2SO_4

Arsenic

I.D. Number	Name
7228100	$FeAsO_4 \cdot 2H_2O$
7215000	$Ca_3(AsO_4)_2 \cdot H_2O$
7231000	$Cu_4(AsO_4)_2 \cdot 6H_2O$
7210000	$Ba_3(AsO_4)_2$
7247000	$Mn_3(AsO_4)_2 \cdot H_2O$
7254000	$Ni_3(AsO_4)_2 \cdot 8H_2O$
7260000	$Pb_3(AsO_4)_2$
7290000	$Zn_3(AsO_4)_2 \cdot 2.5H_2O$

is an absolute requirement. Fortunately the pH is a commonly measured parameter for almost all natural waters.

Eh (pE)--

Eh is an important parameter for elements that have oxidation states linked by redox reactions such as: Fe, Mn, Cu, As, and U. Unfortunately Eh is seldom measured, and what data are available are usually only qualitative. If measured Eh values are available, they should be used but remember their qualitative significance.

There are numerous techniques for estimating the Eh: from solid-solid reactions, from dissolved oxygen concentrations, from analytical data for two oxidation states of an element or from the general concentrations of redox sensitive elements such as Fe and Mn. Some of these techniques, such as analytical data for Fe(II) and Fe(III), may work well. However, no general guidelines can be presented for estimating Eh in all environmental systems. Eh estimates should be made on a case by case basis. If the elements Fe, U, and As are not being considered it is probably better not to estimate an Eh.

Temperature--

Temperature is a required input and must be in degrees Celcius. It is not a sensitive parameter, however. If the input values are within a few degrees Celcius of the actual value, significant errors will usually not result.

Ionic Strength--

The ionic strength is an optional input. Ionic strength will be correctly computed by MINTEQ if concentrations of dominant cations and anions are provided. Computing ionic strength is preferable since a more accurate aqueous speciation is also computed. This also allows the ionic strength to vary as solids precipitate or dissolve. However, if analyses for the dominant cations and anions are not available, the ionic strength can be estimated from specific conductivity (Lindsay 1979). In this case ionic strength can be supplied to MINTEQ and activity coefficients can be computed.

Major Anions--

Included in this category are Cl^-, CO_3^{2-} or alkalinity, SO_4^{2-} and H_4SiO_4. The most important of these are CO_3^{2-} and SO_4^{2-} because they generally form strong complexes and precipitates with most major cations and trace metals. Dissolved silica is also important because it can form several insoluble precipitates but generally does not form significant aqueous complexes with any cations except H^+. Chloride generally forms weak aqueous complexes. Chloride precipitates are generally very soluble and become important only as the chloride concentration approaches that of seawater. There are, however, exceptions to the rule. Silver and copper can form strong chloride complexes whose precipitates are fairly insoluble.

Major Cations--

Included in this category are Ca^{2+}, Mg^{2+}, Na^+, and K^+. The most important of these are Ca^{2+} and Mg^{2+} because they form fairly strong aqueous complexes and insoluble precipitates with anions such as: CO_3^{2-}, SO_4^{2-}, PO_4^{3-} and F^-. They are, therefore, important in obtaining a reliable aqueous speciation. Ca^{2+} generally forms the strongest complexes and is, therefore, somewhat more important than Mg^{2+}.

Na^+ and K^+ are generally important only at high concentrations. However they can be constituents of some relatively insoluble solid phases, such as jarosites.

Trace Constituents--

Hydrogen sulfide (H_2S)--Hydrogen sulfide is extremely important in the geochemistry of trace metals (such as: Fe, Mn, Cu, Zn, Cd, Pb, and Ag), because sulfide forms strong complexes and highly insoluble precipitates with these metals. If the environmental system is reducing, H_2S analysis will be extremely important for accurately predicting trace metal concentrations.

Ortho phosphorus (PO_4^{3-})--Phosphorus is often analyzed as total phosphorus, hydrolyzable phosphorus or ortho phosphorus. Ortho phosphorus is the important form for geochemical modeling. PO_4^{3-} analysis is most important when considering trace metals or Fe, Ca and Mg. PO_4^{3-} forms strong complexes and insoluble precipitates with Fe, Ca and Mg. Because PO_4^{3-} also forms several insoluble trace metal precipitates, it is important in the geochemistry of trace metals, especially Pb and Mn.

Fluoride(F^-)--Fluoride forms several aqueous complexes and solid phases with trace metals. However, fluoride concentrations are generally low, and fluoride will not effect the general geochemistry of the trace metals. However, if fluoride concentrations exceed a few mg/ℓ, significant complexation of trace metals can occur.

Iron and manganese--Except under low pH or Eh conditions, iron and manganese generally do not affect the chemistry of the major cations. However, iron forms strong aqueous complexes with several ligands, such as H_2S and PO_4^{3-} which in turn also form strong complexes with trace metals such as Cu, Zn, and Pb. Therefore, dissolved iron analysis will be important in computing the correct trace metal aqueous speciation. The aqueous complexes of Mn^{2+} are generally much weaker than the Fe complexes and generally not as important.

Aluminum--Dissolved Al is generally important only in the geochemistry of silica, fluoride and phosphorus.

Barium and strontium--Ba^{2+} and Sr^{2+} are usually important only if these constituents are being specifically considered. However, Sr^{2+} is occasionally present in high concentrations and in such cases can effect the aqueous speciation of other constituents especially Ca^{2+} and Mg^{2+}.

Others--The constituents Cs^+, Li^+, Br^-, B, NH_4^+, Rb^+, I^- and NO_3^- are important only in somewhat unusual circumstances. However B can be important in the geochemistry of fluoride and is probably the most important component of this group for computing aqueous speciation.

DATA INPUT TO MEXAMS USING MISP

The MEXAMS Interactive Software Program (MISP) queries the user to obtain two types of information: 1) user run information and 2) MINTEQ input data. The user run information determines which simulation mode will be used (i.e., MINTEQ only, EXAMS only or MINTEQ coupled with EXAMS). It also controls how the simulation results are tranferred back-and-forth between MINTEQ and EXAMS. The MINTEQ input data describe the physical and chemical characteristics within each compartment or set of compartments.

MINTEQ input files can be created by MISP in the MINTEQ only mode or prepared directly with the information given in Appendix C. Before entering the MINTEQ-EXAMS mode all necessary MINTEQ input files must have been created.

In developing MISP, it was assumed that most users would be familiar with the relatively straightforward procedures for creating an EXAMS input file. The input data file for EXAMS contains an execution data set, a toxic chemical database, and an environmental database. As mentioned previously, no changes have been made to the manner in which data is entered in the input data file. The only stipulation is that one must select the heavy metal option, HVM, from the toxic chemical database when using the coupled MINTEQ-EXAMS mode of simulation. The user is referred to the EXAMS user manual and system documentation report for detailed descriptions of the input file procedures. Therefore, MISP does not query the user to create an EXAMS input file. It does, however, request the name of the file the user desires to use and transfers it to EXAMS.

If the coupled MINTEQ and EXAMS mode has been selected, then the following questions will be asked.

Question No. 1: Select the metal ID from the following table.

Select the appropriate ID number from the list provided.

Question No. 2: How many MINTEQ input files will be needed?

Some of the compartments chosen for the EXAMS run may require different MINTEQ water quality data. For example, the basic water quality in a river may change as a result of an industrial discharge or at the confluence of a major tributary. Different MINTEQ input files would then be needed for these compartments.

Question No. 3: Enter no. of compartments for file n.

This question will be asked for each MINTEQ file. Enter number of compartments the water quality data should be applied to.

Question No. 4: Enter compartment numbers for file n.

The actual compartment numbers for each MINTEQ file should be entered.

Question No. 5: How many times do you want to use MINTEQ to update the steady state metal concentrations?

EXAMS initially assumes all of the metal is dissolved. By providing these EXAMS results to MINTEQ, MINTEQ will recalculate the proper dissolved, sediment-sorbed, biosorbed, and precipitated metal concentrations. EXAMS will then use these updated values of metal fractions in another simulation of the transport and fate of the metal in the aquatic environment. This MINTEQ-EXAMS interaction will be repeated the number of times specified in this question.

Question No. 6: How often do you want to use MINTEQ for persistence computations?

Select option number from the following list

(1) every time
(2) every other time
(3) every third time
(4) every fourth time
(5) every fifth time
(6) no persistence update

After the steady-state metal computations are computed, EXAMS will then terminate the loadings of metal to the aquatic environment and calculate subsequent reduced metal concentrations 12 times for an indication of metal persistance. EXAMS will pause a specified number of times to obtain updated dissolved, sediment-sorbed, biosorbed and precipitated metal concentrations from MINTEQ. The above options allow the user to specify the number of times this will occur.

Question No. 7: Select MINTEQ output option.

Three choices will be provided:

1. full MINTEQ printout
2. aqueous species distribution and all mass totals
3. all mass totals

Option one will allow the full MINTEQ printout for every compartment updated by MINTEQ. Option two will only print the dissolved, adsorbed and precipitated totals and a listing of the important dissolved or adsorbed species. Option three just prints the dissolved, adsorbed and precipitated totals. Option one can result in a large volume of output so unless a detailed description of the chemistry of the system is required, options two or three should be selected.

Question No. 8: Enter name of MINTEQ input file n.

If all MINTEQ files are ready, then Question No. 8 will be asked for each file, and each file will be copied in sequential order to the MINTEQ input file named MINTEQ.INP.

Question No. 9: Enter EXAMS input file name.

MISP will copy the EXAMS input file to another file named FOR005.DAT which is used by EXAMS.

The remainder of this discussion focuses on the series of questions MISP poses to the user when creating MINTEQ input files in the MINTEQ only mode. Each question is presented in the same sequence as they would appear on a computer terminal along with a brief discussion of the type of response that should be provided.

When the user executes MISP to create MINTEQ input files in the MINTEQ only mode, the following questions must be answered:

Question No. 1: Enter title of simulation

This line is for entering any identifying run specific information. Any description can be entered to help differentiate this run from other MINTEQ runs. The description must be less than 80 characters.

Question No. 2: Enter description of water body

This provides space for similar descriptive information as question one. Enter whatever identifying information is appropriate for this run. The description must be less than 80 characters.

Question No. 3: Select data units

There are four options: milligrams per liter (mg/ℓ), parts per million (ppm), molality or molarity (MOL) and milliequivalents per liter (meq/ℓ). The units selected should be those used in the water analysis report. An exception is alkalinity. MISP accepts alkalinity in milligrams per liter as $CaCO_3$ and then converts it to the units designated here expressed as CO_3^{2-} before writing the MINTEQ data file.

Question No. 4: Enter Temperature (DEG. CENTIGRADE)

Enter the water temperature in degrees celcius. If you do not give a value, MINTEQ will assume 0°C.

Question No. 5: Will the ionic strength be input?

This option should be selected only if analyses of the dominant cations and anions are not available. In such cases ionic strength can sometimes be estimated from specific conductivity (see the data requirements section). If this option is selected the program will ask for the ionic strength.

Question No. 6: Do you have either a measured pH or a value for the TOTAL H^+?

If you have a measured pH MISP will make all necessary type changes. The TOTAL H^+ stands for "total ionizable H^+". You will very seldom know TOTAL H^+ unless you are dealing with well defined laboratory systems or have made a previous MINTEQ run with a fixed pH in which case MINTEQ will have computed TOTAL H^+. In the latter case TOTAL H^+ can be used to compute the pH.

Question No. 7: If solids are selected to dissolve or precipitate do you want to allow the pH to vary?

This option will allow the pH to change in response to solids dissolving or precipitating. For this option to work all solids must have originally been made Types V. This option is generally useful only in the MINTEQ only mode when studying the water chemistry of the system.

Question No. 8: Do you have an Eh value or do you want to enter the electron as a component?

If you do have a measured or estimated Eh the program will convert the Eh to pE and make all necessary type changes. Entering the electron as a component without having a measured Eh is only useful in cases where the mass total of individual oxidation states of an element are known. For example, analytical data may be available for iron in both oxidation states II and III. In such cases the electron should be entered as a component and the corret pE will be computed.

Question No. 9: Do you have a total alkalinity measurement? (Y or N)

If a measurement of total alkalinity is available, the program will ask for the alkalinity expressed as mg/L $CaCO_3$. The program will convert mg/L $CaCO_3$ to the units you have designated in Question 3 expressed as CO_3^{2-}. Next, MISP will ask for a guess at the log activity of CO_3^{2-}. Log activity of CO_3^{2-} will normally be between -4.0 and -8.0, depending upon such factors as pH and the total alkalinity. If you do not enter a guess the model will default to the analytical input divided by 100.(a)

Question No. 10: Do you have a measurement of total inorganic carbon? (Y or N)

If you do have a TIC measurement the program will ask for the total mass in the units designated in Question 3, expressed as CO_3^{3-}. The program will then ask for a guess at the log activity of CO_3^{2-}. The same concepts described in Question 9 also apply here relative to guessing the CO_3^{2-} activity.

(a) If a solid phase containing CO_2^{3-} is in equilibrium with the solution alkalinity should not be input. In such cases a modeling run should be made with alkalinity input and solids not in equilibrium. This modeling run will result in the computation of total inorganic carbon (TIC). Another modeling run should then be made with TIC input and solids in equilibrium.

Question No. 11: How many iterations will you allow?

The options are:

1. 40
2. 10
3. 100
4. 200

The 100 or 200 iteration options should be selected if a large number of solids will be designated as considered solids (i.e., Type V). The ten iteration option is only useful when debugging the program. If you are not going to allow solids to dissolve or precipitate, the 40 iteration option should be selected.

Question No. 12: Do you want to override the charge balance criteria?

If this option is selected MINTEQ will terminate execution if the initial charge imbalance between input cations and anions is greater than 30%.(a) This is a useful criteria since a large charge imbalance may be an indication that one or more important constituents is missing from the water analysis data. However, there are cases where this criteria should not be applied. If for example, when the user has very limited environmental data, such as only the pH and total cadmium, and wishes to gain some information about the system, he may ignore the charge imbalance. The second case may be when the initial imbalance is very large due to the arbitrary assigning of all the constituent mass to a component such as CO_3^{2-} when actually the solution is predominantly HCO_3^-. In such cases the initial charge balance checked here will exceed the criteria but the final aqueous speciation will be within the criteria. In such cases the charge balance criteria should not be considered.

(a) The actual criteria is $[(\Sigma \text{ anion} - \Sigma \text{ cations})/(\Sigma \text{ anions} + \Sigma \text{ cation})] < 0.3$.

Question No. 13: Do you want to allow all solids in the data base to precipitate if they are oversaturated?

This is one of the most important questions in MISP. If you allow all solids in the data base to precipitate then MINTEQ will check the saturation indices for all the solids in the data base and select the thermodynamically stable solids from these. If you do not allow consideration of all solids, MINTEQ will select the thermodynamically stable solids from the considered solids entered later in this program in Question No. 51. It is recommended that the user carefully read the discussion on the selection of solids in Section 5, Guidelines for Use, before answering this question.

If you decide to consider all solids in the data base you will be asked to select when you want the results printed, the options are:

1. print the results only after all solids are in equilibrium or undersaturated and the problem is completely solved,
2. print the results after the aqueous speciation problem is solved and again after all solids are undersaturated,

3. print the results every time a solid is selected to dissolve or precipitate.

If you are just beginning to use the model and are only interested in the final chemistry of the solution, select option one. Options two and three are only useful if the user is interested in analyzing the chemistry in more detail.

Question No. 14: Enter debug output option number?

This option is useful only when MINTEQ is being made operational on different computers or when the user is interested in very specific chemical or numerical processes. All other times the No Debug option should be selected. The Debug option is described in detail in Appendix C.

Question No. 15 Do you want to use the modified line search and Newton-Raphson iteration?

The user should answer 'no' to this question for all cases except when the problem has been run previously and the iteration did not converge. In such cases the modified line search may be tried. The user should consult the MINTEQ technical document before using the modified line search.

Questions Nos. 16 through 45:

This series of questions asks for the water analysis data. If adsorption is not being considered, enter the total dissolved concentration of all constituents for which water analysis data are available. If adsorption is being considered, the dissolved plus adsorbed concentrations should be entered for every constituent for which adsorption parameters are available. The concentration should be in the units chosen in Question 3 and expressed as the chemical formula shown in the question. As examples, cadmium should be expressed as Cd and boron expressed as H_3BO_3. For every constituent in the water analysis, the program will ask for a guess at the log of the activity of the component. If you do not make a guess at the component activity, the model will default to the analytical concentration divided by 100. Activity guesses are generally important only if model convergence is a problem. Convergence will generally be a problem with components such as Fe^{3+}, U^{+4}, U^{+3}, or H_3AsO_4, where component activity is very small in relation to the total mass of the constituent. In such cases, in oxidizing conditions, a guess of -15.0 to -20.0 will usually work.

Several questions will ask for specific information on each oxidation state of an element. If only the total concentration of that element is available and the user wants to consider the other oxidation states, then the total concentration should be entered as the oxidation state expected to be dominant and the other oxidation states should be included and assigned a mass of zero. In such cases remember to enter the appropriate redox reactions in Question 44.

Question 46: Do you want to consider adsorption?

If you are considering adsorption you will be asked if you want to consider any of the following five adsorption models:

1. "activity" Kd
2. ion exchange
3. "activity" Langmuir

4. constant capacitance model (CCM)
5. triple layer site binding model (TLM)

Regardless of which option is selected, the next question will ask if two different surface sites will be considered. Different surface sites will only be important for laboratory experiments using the constant capacitance and triple layer models or if two different adsorbing substrates are being considered. An example of the latter case would be when "activity" Kd values are available for two different size fractions of suspended material. The majority of the time only one site will be considered.

"Activity" Kd--

If the "activity" Kd option is selected, the following information must be provided:

- Reaction ID Number. The first three digits must be 990 or if two sites are being considered 990 or 991. The next three digits should be the ID number of the adsorbing component. Component ID numbers are given in Table 3. The last digit can be any number 0-9.

- Reaction Name. Select any appropriate identifying name. The name must be less than 12 characters.

- "Activity" Kd. This is the distribution coefficient written in terms of the activity of the component.

Next provide the ID numbers for the adsorbing components and the ID for either surface site one (990) or surface site two (991), if two sites are being considered. All necessary type changes will be made by the program.

Ion Exchange--

If the ion exchange algorithm is selected, the following information must be provided:

- Reaction ID Number. For ion exchange any seven digit number can be selected which is not already in the data base. It is recommended the first six digits be the ID numbers for the exchanging components and the last digit be any number 0-9. This ID selection will insure the number is not already in the data base.

- Reaction Name. Select any appropriate identifying name. The name must be less than 12 characters.

- Exchange Constant. Enter the logarithm of the Exchange Constant.

MISP will next ask for the ID numbers for the exchanging components and their stoichiometries. Remember if a component is on the right side of the exchange reaction the stoichiometry will be negative.

"Activity" Langmuir Isotherm--

If the "activity" Langmuir isotherm is selected, the following information must be provided.

- Reaction ID Number. The first three digits must be 990 or if two sites are being considered 990 or 991. The next three digits should be the ID number for the adsorbing component. The last digit can be any number 0-9.

- Reaction Name. Select any appropriate identifying name. The name must be less than 12 characters.

- "Activity" Langmuir Constant. This is the Langmuir constant obtained by using the activity of the uncomplexed component instead of the total concentration.

- Total Surface Coverage. This is the total surface sites obtained by using the activity of the uncomplexed component instead of the total concentration.

Next provide the ID number for the adsorbing component and the ID number for either surface site one (990) or surface site two (991). All necessary type changes will be made by the program.

Constant Capacitance or Triple Layer Models--

Regardless of which of these two models is selected the following information will be required:

- total surface sites of adsorbent (sites/g)
- guess at the surface potential (PSIO)

- concentration of adsorbent (g/L)
- specific surface area of adsorbent (m^2/g)
- inner layer capacitance (Farads/m^2).

The total surface sites must be expressed in sites/gram. The concentration of adsorbing solid (suspended solids) must be in grams/liter, specific surface area in square meters per gram, and the capacitance in Farads per square meter. The necessary experimental or literature data are described in the MINTEQ technical report. Estimates of the surface potential are difficult to make but a guess in the range of -0.2 to -4.0 will probably work. The inner layer capacitance is usually about 1.4.

If the triple layer model is selected the following additional information must be provided:

- outer layer capacitance (F/m^2)
- guess at the potential at the beta plane (XPSIB)
- guess at the potential at the diffuse plane (XPSID)

The outer layer capacitance is normally around 0.2 Farads/square meter. The guesses at the potentials are difficult to make but -0.2 to -4.0 should normally work.

After providing the necessary adsorption parameters for the constant capacitance or triple layer models the user must provide information for each adsorbing species.

- I.D. number
- equilibrium constant

- number of reaction components and the stoichiometry and ID for each component.

The ID number was previously described under activity Kd. The equilibrium constants and reaction component information must be evaluated from experimental or literature data. The user is referred to the MINTEQ technical document for more detailed information on the constant capacitance and triple layer models.

Question No. 47: Do you want to enter any redox reactions?

Redox reactions relate the activities of two components. If the user has only a total elemental analysis and wishes to consider the different oxidation states of the element, the redox reactions between the different components must be included here. As an example if only an analysis of total dissolved iron is available and the user wishes to consider both Fe(II) and Fe(III), then the redox reaction between Fe^{2+} and Fe^{3+} must be included, ID number 2812800. Remember if redox reactions are included all of the components (i.e., in this example Fe^{2+} and Fe^{3+}) must be entered in Questions 16 through 45 and either the Eh must be entered or the electron included as a component. If redox reactions are included, the program will ask if new thermodynamic data (i.e., new equilibrium constants or heat of reaction) are available. The user should answer "No" to these questions unless more recent and reliable thermodynamic data are available. If new data are available the user will be queried for the new equilibrium constants or enthalpy of reaction.

Question No. 48: Do you want to include gases at a fixed partial pressure?

The gas phases in the MINTEQ thermodynamic data base are listed in Table 8.

If the user selects one of these gases the program will ask for the equilibrium constant modified for the partial pressure of the gas (see the discussion on Type Modifications). All necessary type changes will be performed by MISP.

Question No. 49: Do you want any solids to be present regardless of how much may dissolve?

The solids selected here will be imposed on the aqueous solution and will modify the solution composition. The model will dissolve or precipitate as much solid as required to equilibrate the solution. The solid I.D. numbers are given in the thermodynamic data base of the MINTEQ technical document.

Question No. 50: Do you want to include solids which are only allowed to dissolve a specified amount

The solids selected here will only be allowed to dissolve some initial specified mass plus any mass that may precipitate from solution during the

TABLE 8. GAS PHASES IN MINTEQ

Gas	I.D. Number
Methane (CH_4)	3301404
Carbon Dioxide (CO_2)	3301403
Oxygen (O_2)	3300023

computations. If any solids are selected here the user will be asked to provide the initial solid concentrations in moles/liter. The user will also be asked if more recent thermodynamic data such as a new equilibrium constant or enthalpy of reaction are available. The solid I.D. numbers can be found in the thermodynamic data base in the MINTEQ technical document.

Question No. 51: Are there any solids that you will allow to precipitate if they become oversaturated?

This question allows the user to input a list of "considered" (Type V) solids. If any of these solids become oversaturated MINTEQ will select the thermodynamically stable phases from the solids listed here and adjust the solution composition to equilibrium with these solids. Before designating solids, the user should read the Guidelines for Use Section, Selection of Solids. If the user has more reliable thermodynamic data, such as a new equilibrium constant or enthalpy of reaction, for any of these solids these data can be entered here. This question will only be asked if a "no" response was given to Question 13.

Question No. 52: Are there are species you do not want to consider during the equilibrium computations?

This question is most useful for removing certain Type V solids from consideration when all solids in the data base are being considered and for selectively not considering certain aqueous complexes in the geochemical calculations. The only other major importance of this question is in allowing the pE to vary during the precipitation of solid phases. In such cases the electron must be included as a Type VI species here. For further details on variable pE during precipitation or dissolution of solids consult the MINTEQ technical manual.

Question No. 53: Do you want to change the equilibrium constant or heat of reaction for any species in the data base which this program has not already changed?

This catch-all type question is useful only to users with very specific problems that cannot be adequately answered in previous questions. Generally only experienced users of the program will find this question useful.

Question No. 54: Do you want to add species to the data base for this run only?

Any species can be added at this point except new components. To add new components the thermodynamic data files must be modified. If the user wishes to add species for this run the program will ask for the following information:

- I.D. number
- reaction name
- enthalpy of reaction
- equilibrium constant (log K)
- minimum log K
- maximum log K
- species charge
- Debye-Huckel A and B parameter
- molecular weight

- carbonate alkalinity factor
- stoichiometry and I.D. number for all reaction components.

Only the I.D. number, log K and reaction component information are absolutely necessary. The carbonate alkalinity factor is valid only for aqueous species containing carbonate as a component. All of the parameters listed here are described in the MINTEQ technical document.

There can occasionally be problems in determining species I.D. numbers for inserted species added here. Appendix C gives a detailed description of how to determine the correct I.D. numbers.

Question No. 55: Do you want to check your constituent entries?

The information for the components can be printed to allow careful checking before MINTEQ initiates the geochemical calculations or stores the data in a file.

INTERPRETATION OF MEXAMS OUTPUT

MEXAMS provides the user with three sets of simulation results: 1) details on metal speciation, sorption and precipitation in each compartment, 2) exposure, fate and persistence predictions for the aquatic system and 3) a summary of the MINTEQ-EXAMS interactions. The first set of results are provided by MINTEQ; the second set is provided by EXAMS and the third set by MISP. The EXAMS users manual and documentation report provides a detailed description of the EXAMS output. The only change is the addition of the quantity of precipitated metal to the tables that summarize model results. This discussion presents the types of output and error messages generated by MISP and MINTEQ.

The MISP output summarizes the MINTEQ-EXAMS interaction. It contains a listing of metal concentrations in dissolved adsorbed and precipitated form before and after the various MINTEQ updates. This information shows the effect of each MINTEQ update. The final metal concentrations are printed in the EXAMS output.

MINTEQ Output

The MINTEQ output is divided into several sections. MISP allows the user to specify which of these sections MINTEQ will generate for each compartment MINTEQ solves in the MINTEQ-EXAMS mode. The options available to the user and the information contained in each section are described below. Examples of actual output are provided for reference. The terms used in the MINTEQ output are defined in Table 9.

If the user selects the linked MINTEQ and EXAMS mode, then MISP will ask the user for a MINTEQ output option for each compartment. There are three options:

(1) regular MINTEQ output
(2) print only the distribution of aqueous species and the mass dissolved, precipitated or adsorbed
(3) print only the mass dissolved, precipitated or adsorbed.

The regular MINTEQ output is described in the following sections. If the user selected option (1) Sections 1-6 of the following section will be printed. If option (2) is selected only the percentage distribution of

TABLE 9. DEFINITION OF TERMS USED IN THE MINTEQ OUTPUT

DH - enthalpy of reaction

DHA - Debye Huckel A parameter

DHB - Debye Huckel B parameter

DIFF FXN - the difference between the analytical total and the sum of all aqeous and adsorbed species calculated by the model

GAMMA - activity coefficient

GFW - gram formula weight

LOG AP/K - log saturation index

LOG IAP - log ion activity product

NEW log K - equilibrium constant corrected for temperature and ionic strength

TOTAL MOL - total concentration in molality

Z - species charge

ANAL MOL - total analytical molality

CALC MOL - calculated species molality

components in Section 5 and the mass total summary in Section 6 will be printed. If option (2) is selected only the mass total summary in Section 6 will be printed.

Section 1--

The first output is of the original sample description file. Certain explanatory statements are frequently printed here to inform the user of any changes the model has made to the original sample description. These messages are self explanatory. For example, "H_2O HAS BEEN INSERTED AS A COMPONENT" is always printed. The purpose of this section is to allow the user to examine the input sample file to check for errors. A listing of the input sample file is given in Appendix C. The first page of the output for this section is given in Table 10. A detailed description of Table 10 can be found in Appendix C.

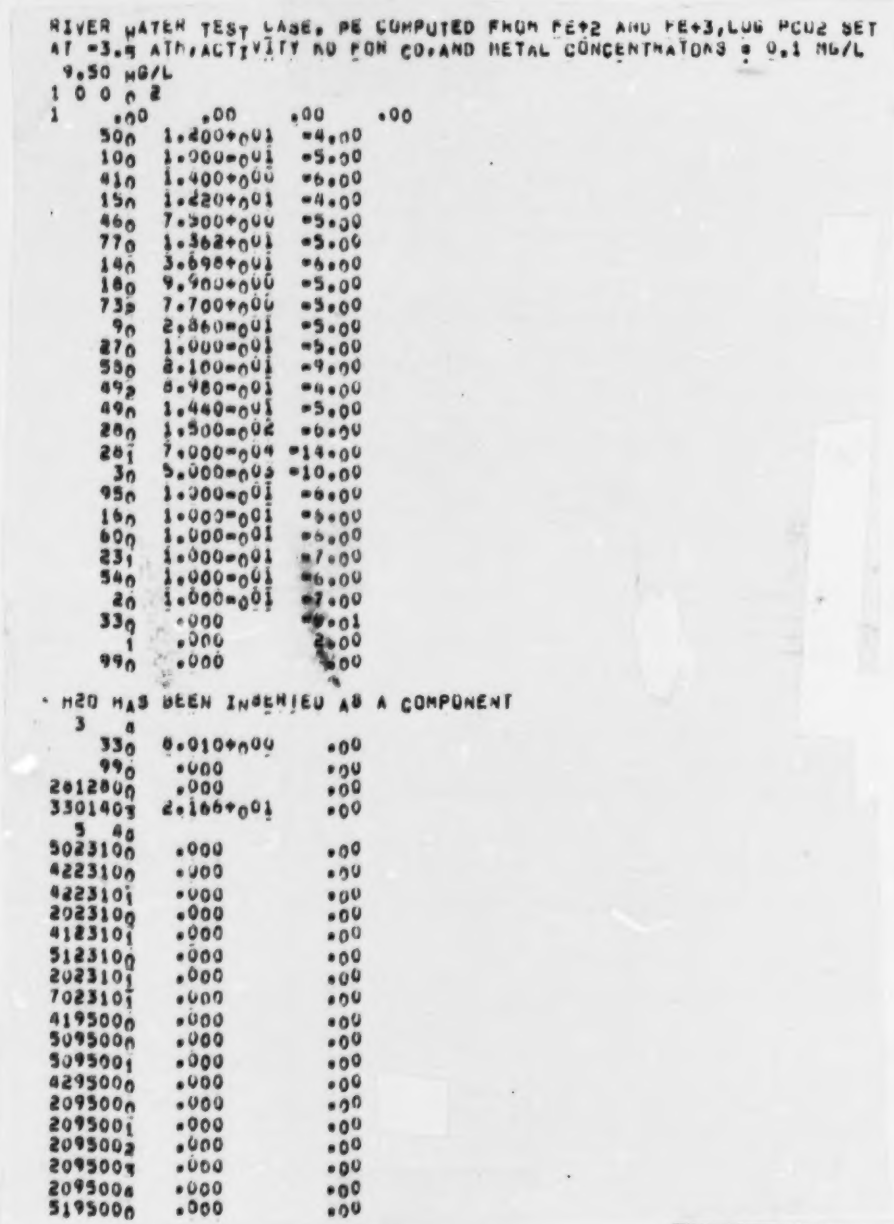
Section 2--

This section prints the thermodynamic and accessory data for all species except for default Type VI solids. Default Type VI solids are printed separately under "SATURATION INDICES FOR ALL MINERALS AND SOLIDS". The meaning of the column headers is defined in Table 9. The purpose of this section is to print the initial starting information before MINTEQ initiates the geochemical calculations. Table 11 is a copy of the first page of output for this section.

Section 3--

This section provides the initial charge balance information before aqueous speciation. The sum of cation and anions is printed in milliequivalents per liter. A large charge imbalance can be an indication that one or more major components was not included in the water analysis. However, occasionally the water analysis will include all necessary components and the initial charge imbalance will still be large. This commonly occurs when the alkalinity (or HCO_3^- and CO_3^{2-}) are the dominant anions. The charge on the entire mass of inorganic carbon is given as minus two since CO_3^{2-} is the component. If the inorganic carbon is really all HCO_3^-, this can create a computational charge imbalance. Therefore, the importance of

TABLE 10. SECTION ONE OF THE MINTEQ OUTPUT



```
RIVER WATER TEST CASE, PE COMPUTED FROM FE+2 AND FE+3,LOG PCO2 SET
AT -3.5 ATM,ACTIVITY NO FOR CO,AND METAL CONCENTRATONS = 0.1 MG/L
 9.50 MG/L
1 0 0 0 2
1     .00     .00     .00     .00
     500  1.200+001   -4.00
     100  1.000-001   -5.00
     410  1.400+000   -6.00
     150  1.220+001   -4.00
     460  7.500+000   -5.00
     770  1.362+001   -5.00
     140  3.698+001   -6.00
     180  9.900+000   -5.00
     732  7.700+000   -5.00
      90  2.860-001   -5.00
     270  1.000-001   -5.00
     550  8.100-001   -9.00
     492  8.480-001   -4.00
     490  1.440-001   -5.00
     280  1.500-002   -6.00
     281  7.000-004  -14.00
      30  5.000-005  -10.00
     950  1.000-001   -6.00
     160  1.000-001   -6.00
     600  1.000-001   -6.00
     231  1.000-001   -7.00
     540  1.000-001   -6.00
      20  1.000-001   -7.00
     330   .000       -8.01
       1   .000        2.00
     990   .000         .00
 * H2O HAS BEEN INSERTED AS A COMPONENT
   3   8
     330  8.010+000      .00
     990   .000          .00
 2012800   .000          .00
 3301403  2.166+001      .00
   5  40
 5023100   .000          .00
 4223100   .000          .00
 4223101   .000          .00
 2023100   .000          .00
 4123101   .000          .00
 5123100   .000          .00
 2023101   .000          .00
 7023101   .000          .00
 4195000   .000          .00
 5095000   .000          .00
 5095001   .000          .00
 4295000   .000          .00
 2095000   .000          .00
 2095001   .000          .00
 2095002   .000          .00
 2095004   .000          .00
 2095006   .000          .00
 5195000   .000          .00
```

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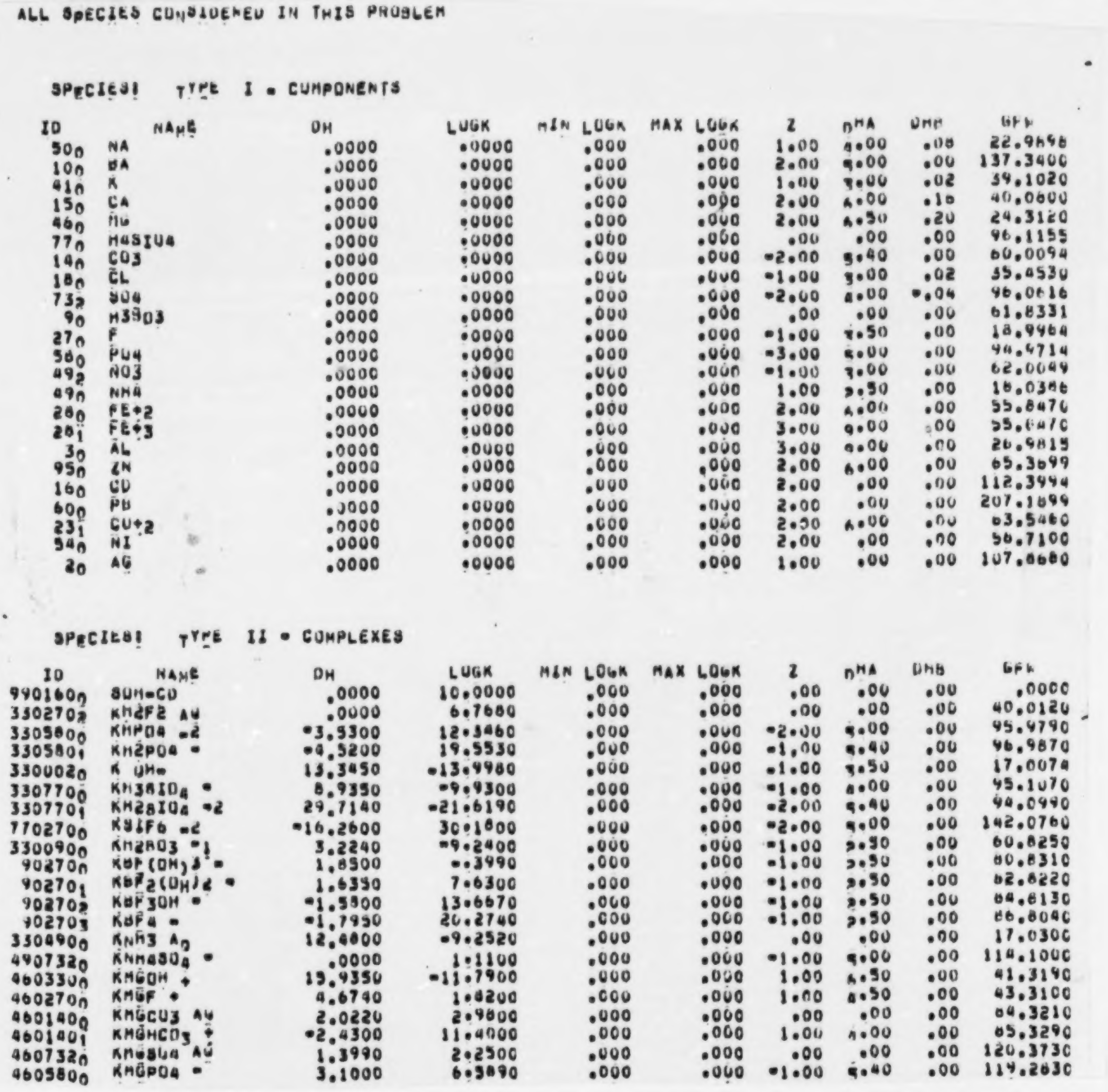
TABLE 11. SECTION TWO OF THE MINTEQ OUTPUT



```
ALL SPECIES CONSIDERED IN THIS PROBLEM


  SPECIES:   TYPE  I - COMPONENTS

 ID        NAME            DH          LOGK    MIN LOGK  MAX LOGK    Z     DHA    DHB      GFW
  500  NA               .0000         .0000       .000      .000   1.00   4.00   .08   22.9898
  100  BA               .0000         .0000       .000      .000   2.00   5.00   .00  137.3400
  410  K                .0000         .0000       .000      .000   1.00   3.00   .02   39.1020
  150  CA               .0000         .0000       .000      .000   2.00   6.00   .16   40.0800
  460  MG               .0000         .0000       .000      .000   2.00   6.50   .20   24.3120
  770  H4SIO4           .0000         .0000       .000      .000    .00    .00   .00   96.1155
  140  CO3              .0000         .0000       .000      .000  -2.00   5.40   .00   60.0094
  180  CL               .0000         .0000       .000      .000  -1.00   3.00   .02   35.4530
  732  SO4              .0000         .0000       .000      .000  -2.00   4.00  -.04   96.0616
   90  H3BO3            .0000         .0000       .000      .000    .00    .00   .00   61.8331
  270  F                .0000         .0000       .000      .000  -1.00   3.50   .00   18.9984
  580  PO4              .0000         .0000       .000      .000  -3.00   5.00   .00   94.9714
  492  NO3              .0000         .0000       .000      .000  -1.00   3.00   .00   62.0049
  490  NH4              .0000         .0000       .000      .000   1.00   2.50   .00   18.0386
  280  FE+2             .0000         .0000       .000      .000   2.00   6.00   .00   55.8470
  281  FE+3             .0000         .0000       .000      .000   3.00   9.00   .00   55.8470
   30  AL               .0000         .0000       .000      .000   3.00   9.00   .00   26.9815
  950  ZN               .0000         .0000       .000      .000   2.00   6.00   .00   65.3699
  160  CD               .0000         .0000       .000      .000   2.00    .00   .00  112.3994
  600  PB               .0000         .0000       .000      .000   2.00    .00   .00  207.1899
  231  CU+2             .0000         .0000       .000      .000   2.00   6.00   .00   63.5460
  540  NI               .0000         .0000       .000      .000   2.00    .00   .00   58.7100
   20  AG               .0000         .0000       .000      .000   1.00    .00   .00  107.8680


  SPECIES:   TYPE  II - COMPLEXES

  ID       NAME            DH          LOGK    MIN LOGK  MAX LOGK    Z     DHA    DHB      GFW
9901600  SOH-CD           .0000       10.0000       .000      .000    .00    .00   .00     .0000
3302702  KH2F2 AQ         .0000        6.7680       .000      .000    .00    .00   .00   40.0120
3305800  KHPO4 -2       -3.5300       12.3460       .000      .000  -2.00   5.00   .00   95.9790
3305801  KH2PO4 -       -4.5200       19.5530       .000      .000  -1.00   5.40   .00   96.9870
3300020  K OH-          13.3450      -13.9980       .000      .000  -1.00   3.50   .00   17.0074
3307700  KH3SIO4 -       8.9350       -9.9300       .000      .000  -1.00   4.00   .00   95.1070
3307701  KH2SIO4 -2     29.7140      -21.6190       .000      .000  -2.00   5.40   .00   94.0990
7702700  KSIF6 -2      -16.2600       30.1800       .000      .000  -2.00   5.00   .00  142.0760
3300900  KH2BO3 -1       3.2240       -9.2400       .000      .000  -1.00   2.50   .00   60.8250
 902700  KBF(OH)3 -      1.8500        -.3990       .000      .000  -1.00   2.50   .00   80.8310
 902701  KBF2(OH)2 -     1.6350        7.6300       .000      .000  -1.00   2.50   .00   82.8220
 902702  KBF3OH -       -1.5800       13.6670       .000      .000  -1.00   2.50   .00   84.8130
 902703  KBF4 -         -1.7950       20.2740       .000      .000  -1.00   2.50   .00   86.8040
3304900  KNH3 AQ        12.4800       -9.2520       .000      .000    .00    .00   .00   17.0300
4907320  KNH4SO4 -        .0000        1.1100       .000      .000  -1.00   5.00   .00  114.1000
4603300  KMGOH +        15.9350      -11.7900       .000      .000   1.00   6.50   .00   41.3190
4602700  KMGF +          4.6740        1.8200       .000      .000   1.00   4.50   .00   43.3100
4601400  KMGCO3 AQ       2.0220        2.9800       .000      .000    .00    .00   .00   84.3210
4601401  KMGHCO3 +      -2.4300       11.4000       .000      .000   1.00   4.00   .00   85.3290
4607320  KMGSO4 AQ       1.3990        2.2500       .000      .000    .00    .00   .00  120.3730
4605800  KMGPO4 -        3.1000        6.5890       .000      .000  -1.00   5.40   .00  119.2830
```

any charge imbalance should be interpreted on a case by case basis. An example of the output for this section is given in Table 12.

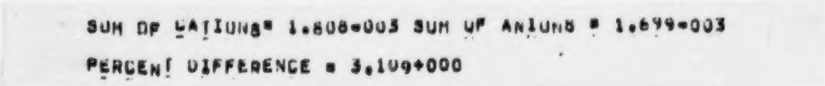
Section 4--

This section prints the convergence pattern as the equilibrium problem is solved. Convergence information is printed only for the first component the model encounters which has not converged. This information is useful only to the experienced user of the model who may be interested in obtaining closer estimates of the component activities to use as initial guesses or is interested in analyzing the Newton-Raphson numerical method. An example of the output for this section is given in Table 13. If convergence is not reached an error message will be printed.

Section 5--

The next printout will begin with: 'OUTPUT DATA', 'PERCENTAGE DISTRIBUTION OF COMPONENTS' or 'SATURATION INDICES FOR TYPE 6 SOLIDS'. The actual order in which these are printed depends upon user input options. Occasionally there is a K before the name of an aqueous species. This convention was used in WATEQ3 to distinguish solid phases from aqueous species and has been retained in MINTEQ for some species. An example is given for each output group in Tables 14 through 16.

TABLE 12. SECTION THREE OF THE MINTEQ OUTPUT



```
SUM OF CATIONS= 1.808-003 SUM OF ANIONS = 1.699-003
PERCENT DIFFERENCE = 3.109+000
```

TABLE 13. SECTION FOUR OF THE MINTEQ OUTPUT

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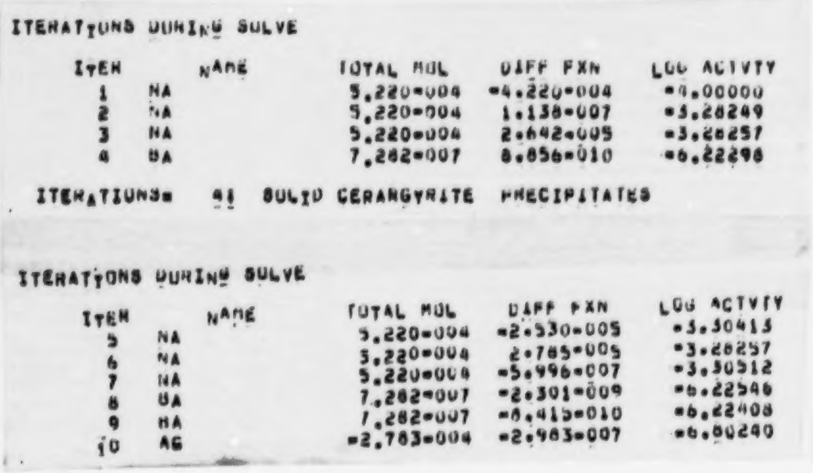

```
ITERATIONS DURING SOLVE

      ITEM        NAME          TOTAL MOL    DIFF FXN     LOG ACTVTY
        1   NA                  5.220-004   -4.220-004    -4.00000
        2   NA                  5.220-004    1.138-007    -3.28249
        3   NA                  5.220-004    2.642-005    -3.28257
        4   UA                  7.282-007    8.856-010    -6.22298

  ITERATIONS=    41  SOLID CERANGYRITE  PRECIPITATES

ITERATIONS DURING SOLVE

      ITEM        NAME          TOTAL MOL    DIFF FXN     LOG ACTVTY
        5   NA                  5.220-004   -2.530-005    -3.30413
        6   NA                  5.220-004    2.785-005    -3.28257
        7   NA                  5.220-004   -5.996-007    -3.30512
        8   UA                  7.282-007   -2.301-009    -6.22546
        9   HA                  7.282-007   -8.415-010    -6.22408
       10   AG                 -2.783-004   -2.983-007    -6.00240
```

Output Data--The following information is printed for species Types I and II.

- molality
- activity
- log activity
- activity coefficient (heading GAMMA)
- log K (modified for both ionic strength and temperature)
- DH (enthalpy of reaction, ΔH°r)

TABLE 14. SECTION FIVE OF THE MINTEQ OUTPUT (OUTPUT DATA:)

```
OUTPUT DATA:  ITERATIONS =  10

 ID        NAME             ANAL MOL   CALC MOL   ACTIVITY    LOG ACTIVTY      GAMMA       NEW LOGK    DIFF FXN
 500  NA                   5.220-004  5.217-004  4.965-004    -3.30412       .951528        .0216   -1.078-009
 100  BA                   7.282-007  7.282-007  5.977-007    -6.22349       .820852        .0857   -5.630-012
 410  K                    3.581-005  3.579-005  3.403-005    -4.46820       .950560        .0220   -7.076-011
 150  CA                   3.044-004  3.000-004  2.472-004    -3.60702       .823766        .0842   -2.281-009
 460  MG                   3.085-004  3.036-004  2.505-004    -3.60118       .825011        .0835   -2.291-009
 770  H4SIO4               1.417-004  1.409-004  1.410-004    -3.85075      1.000493       -.0002   -5.996-012
  20  AG                   9.272-007  1.659-007  1.578-007    -6.80193       .951535        .0217    2.654-010
 540  NI                   1.703-006  1.186-007  9.712-008    -7.01270       .818751        .0868   -1.046-012
 732  SO4                  8.017-005  7.490-005  6.130-005    -4.21257       .818389        .0870   -6.023-010
  90  H3BO3                4.626-006  4.422-006  4.425-006    -5.35413      1.000493       -.0002   -6.133-013
 270  F                    5.264-006  5.200-006  4.944-006    -5.30590       .950836        .0219   -1.086-011
 580  PO4                  2.211-006  6.810-011  4.368-011   -10.35977       .641352        .1929   -1.261-011
 492  NO3                  1.448-005  1.448-005  1.377-005    -4.86116       .950490        .0221   -2.983-011
 490  NH4                  7.984-006  7.843-006  7.452-006    -5.12773       .950139        .0222   -1.578-011
 280  FE+2                 2.486-007  2.638-007  2.172-007    -6.66320       .823097        .0845   -2.035-012
 281  FE+3                 1.254-008  2.406-019  1.580-019   -18.80132       .656669        .1827   -1.617-014
  30  AL                   1.853-007  2.214-015  1.454-015   -14.83751       .656669        .1827   -7.627-014
 950  ZN                   1.530-006  9.725-007  8.005-007    -6.09664       .823097        .0845   -7.888-012
 160  CU                   8.898-007  1.087-016  8.898-017   -16.05072       .818751        .0868    4.108-013
 600  PB                   4.827-007  1.406-008  1.151-008    -7.93889       .818751        .0866   -2.220-013
 231  CU+2                 1.574-006  8.209-009  6.757-009    -8.17026       .823097        .0845    2.534-013
   2  H2O                   .000      5.414-004  1.000+000     -.00002      1.000000        .0000     .000
 990  SOH1                  .000     -8.898-007  1.000+000      .00000      1.000000        .0000     .000
 140  CO3                  1.236-003  2.654-006  2.181-006    -5.66132       .821757        .0853     .000
   1  E                     .000      5.060-002  5.060-002    -1.29583      1.000000        .0000     .000
 330  H                     .000     -1.785-003  9.772-009    -8.01000       .954944       8.0100     .000
 180  CL                   2.793-004  2.785-004  2.647-004    -3.57719       .950560        .0220     .000


SPECIES:   TYPE  I - COMPONENTS

 ID        NAME             CALC MOL    ACTIVITY     LOG ACTIVTY      GAMMA       NEW LOGK        DH
 500  NA                   5.217-004   .0004965     -3.30412       .951528        .022         .000
 100  BA                   7.282-007   .0000006     -6.22349       .820852        .086         .000
 410  K                    3.579-005   .0000340     -4.46820       .950560        .022         .000
 150  CA                   3.000-004   .0002472     -3.60702       .823766        .084         .000
 460  MG                   3.036-004   .0002505     -3.60118       .825011        .084         .000
 770  H4SIO4               1.409-004   .0001410     -3.85075      1.000493       -.000         .000
 140  CO3                  2.654-006   .0000022     -5.66132       .821757        .085         .000
 180  CL                   2.785-004   .0002647     -3.57719       .950560        .022         .000
 732  SO4                  7.490-005   .0000613     -4.21257       .818389        .087         .000
  90  H3BO3                4.422-006   .0000044     -5.35413      1.000493        .000         .000
 270  F                    5.200-006   .0000049     -5.30590       .950836        .022         .000
 580  PO4                  6.810-011   .0000000    -10.35977       .641352        .193         .000
 492  NO3                  1.448-005   .0000138     -4.86116       .950490        .022         .000
 490  NH4                  7.843-006   .0000075     -5.12773       .950139        .022         .000
 280  FE+2                 2.638-007   .0000002     -6.66320       .823097        .085         .000
 281  FE+3                 2.406-019   .0000000    -18.80132       .656669        .183         .000
  30  AL                   2.214-015   .0000000    -14.83751       .656669        .183         .000
 950  ZN                   9.725-007   .0000008     -6.09664       .823097        .085         .000
 160  CU                   1.087-016   .0000000    -16.05072       .818751        .087         .000
 600  PB                   1.406-008   .0000000     -7.93889       .818751        .087         .000
 231  CU+2                 8.209-009   .0000000     -8.17026       .823097        .085         .000
```

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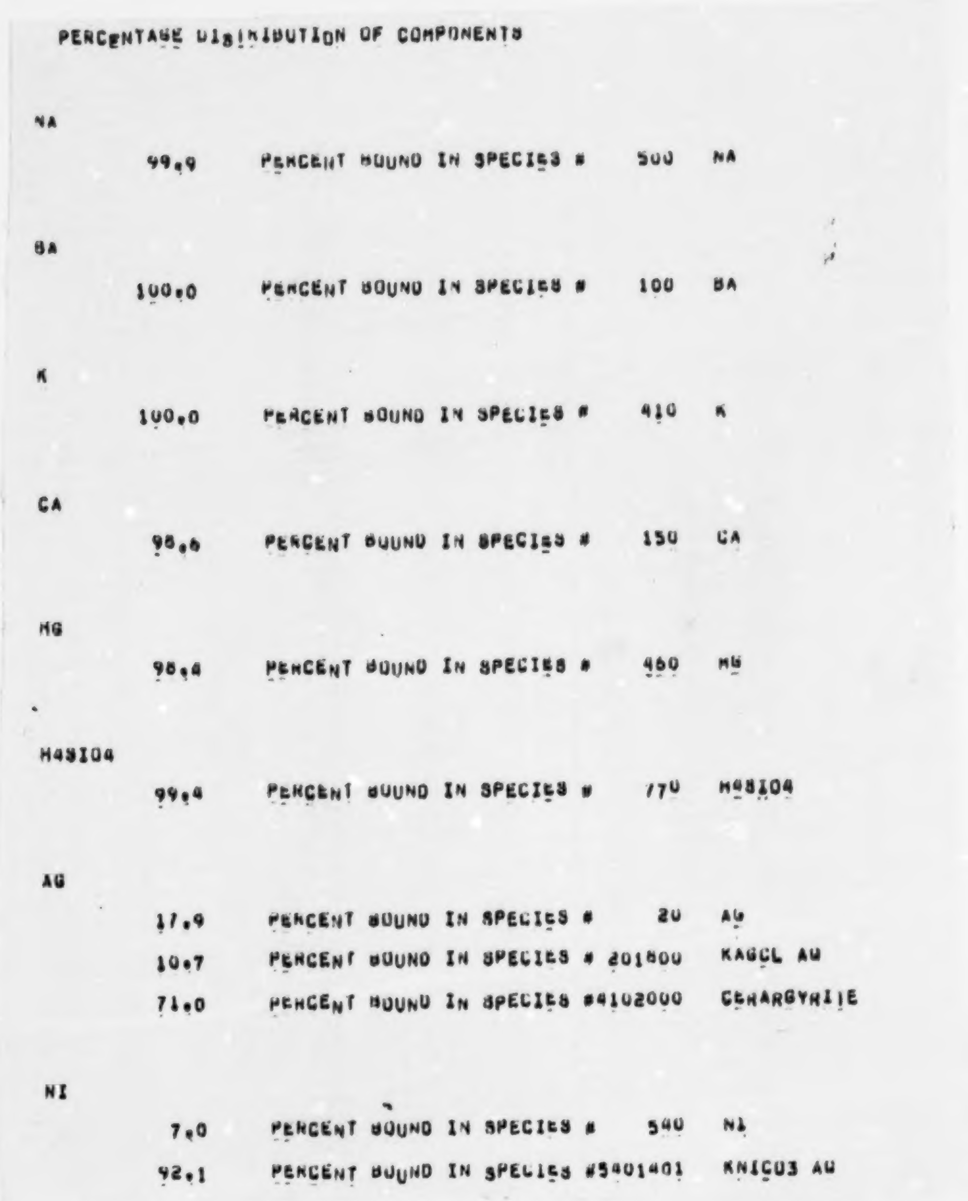
TABLE 15. SECTION FIVE OF THE MINTEQ OUTPUT (PERCENTAGE DISTRIBUTION OF COMPONENTS)



```
 PERCENTAGE DISTRIBUTION OF COMPONENTS


NA
          99.9     PERCENT BOUND IN SPECIES #     500   NA


BA
         100.0     PERCENT BOUND IN SPECIES #     100   BA


K
         100.0     PERCENT BOUND IN SPECIES #     410   K


CA
          98.6     PERCENT BOUND IN SPECIES #     150   CA


MG
          98.4     PERCENT BOUND IN SPECIES #     460   MG


H4SIO4
          99.4     PERCENT BOUND IN SPECIES #     770   H4SIO4


AG
          17.9     PERCENT BOUND IN SPECIES #      20   AG
          10.7     PERCENT BOUND IN SPECIES # 201800   KAGCL AQ
          71.0     PERCENT BOUND IN SPECIES #4102000   CERARGYRITE


NI
           7.0     PERCENT BOUND IN SPECIES #     540   NI
          92.1     PERCENT BOUND IN SPECIES #5401401   KNICO3 AQ
```

TABLE 16. SECTION FIVE OF THE MINTEQ OUTPUT (SATURATION INDICES FOR ALL MINERALS AND SOLIDS)

```
SATURATION INDICES FOR ALL MINERALS AND SOLIDS

   ID     NAME          LOG AP/K    LOG K    MIN LOGK   MAX LOGK   LOG IAP       DH
2003000 ALOH3(A)         -2.275   -11.467   -10.777    -1.087     9.192     27.045
6003000 ALOHSO4          -7.810     3.230     3.390     3.070   -11.040       .000
6003001 AL4(OH)10SO4     -6.163   -22.700      .000      .000    16.537       .000
6041000 ALUM K          -22.271     5.460      .290      .290   -27.731     -7.220
6041001 ALUNITE          -7.842     1.503      .157      .157    -9.346     -3.918
6015000 ANHYDRITE        -3.334     4.486     -.151     -.151    -7.820      3.769
5015000 ARAGONITE        -1.013     8.255     -.105     -.105    -9.268      2.615
5046000 ARTINITE         -7.599   -10.755    -1.155    -1.155     3.136     28.742
4210000 BAF2            -11.035     5.800     6.780     4.690   -16.835     -1.000
6010000 BARITE            -.205    10.228      .252    10.025   -10.436     -6.280
2003001 BOEHMITE          -.516    -9.709    -9.196    -1.131     9.192     28.130
2046000 BRUCITE          -5.412   -17.031    -1.039    -1.039    12.419     25.840
5015001 CALCITE           -.897     8.371     8.456     -.104    -9.268      2.585
2077000 CHALCEDONY        -.142     3.708      .165      .165    -3.851     -4.615
8646000 CHRYSOTILE       -4.743   -34.290    -2.110    -2.110    29.555     52.485
8246000 CLINOENSTITE     -3.574   -12.142   -11.776   -12.436     8.608     20.015
2077001 CRISTOBALITE      -.043     3.808      .221      .221    -3.851     -5.500
2003002 DIASPORE          1.329    -7.863     -.990     -.990     9.192     24.030
8215000 DIOPSIDE         -4.053   -21.183    -1.297    -1.297    17.130     32.280
5015002 DOLOMITE         -1.864    16.667     -.333     -.333   -18.531      8.290
6046000 EPSOMITE         -5.561     2.253      .113      .113    -7.814     -2.820
8646003 SEPIOLITE(C)     -3.724   -17.009    -1.096    -1.096    13.285     27.268
2028100 FERRIHYDRITE       .338    -4.891    -1.597    -4.996     5.229       .000
2028101 FE3(OH)8          -.408   -20.222   -17.112   -24.105    19.814       .000
4128100 FEOH)2.7CL.3      4.792     3.040      .000      .000     1.752       .000
6028100 FE2(SO4)3       -56.197    -5.956    -1.726    -2.376   -50.940     59.120
4215000 FLUORITE         -3.069    11.149      .189      .189   -14.219     -4.710
8046000 FORSTERITE       -9.261   -30.248    -1.950    -1.950    20.987     88.510
2003003 GIBBSITE (C)      -.494    -9.686    -9.403   -10.356     9.192     22.800
2028102 GOETHITE          4.147    -1.082     -.582     -.582     5.929     14.480
8628000 GREENALITE        -.441   -20.810      .000      .000    20.369       .000
6015001 GYPSUM           -2.961     4.858      .010      .010    -7.820      -.261
4150000 HALITE           -8.426    -1.545      .037      .037    -6.881      -.918
3028100 HEMATITE         13.226     2.768    -1.240    -1.240    10.857     30.845
5015003 HUNTITE          -8.123    28.933    -1.035    -1.035   -37.056     25.760
5046001 HYDRMAGNESIT    -17.964     6.667    -2.099    -2.099   -24.631     52.210
6050000 JAROSITE NA     -10.328     9.746    -1.454    -1.454   -20.073     36.160
6041002 JAROSITE K       -7.695    13.543    -1.257    -1.257   -21.237     31.280
6028101 JAROSITE H      -14.696     9.083    -2.217    -2.217   -24.779     55.150
8450000 MAGADIITE        -7.949    14.300      .000      .000   -22.244       .000
3028101 MAGHEMITE         4.071    -6.386      .000      .000    10.457       .000
5046002 MAGNESITE        -1.481     7.781     8.031     7.531    -9.262      6.169
3028000 MAGNETITE        14.049    -5.765    -5.395    -8.623    19.814     50.460
6028000 MELANTERITE      -8.291     2.585      .115      .115   -10.876     -2.860
6050001 MIRABILITE       -8.944     1.877      .763      .763   -10.821    -18.987
3050000 NATRON          -10.326     1.944      .633      .633   -12.270    -15.745
5046003 NESQUEHONITE     -3.874     5.388     4.900     4.313    -9.263      5.789
8646001 PHLOGOPITE      -31.333   -69.771    -3.471    -3.471    38.438     86.360
2077002 QUARTZ             .405     4.256      .250      .250    -3.851     -6.220
8646004 SEPIOLITE(A)     -5.495   -18.780      .000      .000    13.285       .000
5028000 SIDERITE         -1.989    10.336    11.890     -.214   -12.325      5.328
2077003 SIO2(A,GL)        -.654     3.196      .178      .178    -3.851     -4.440
2077004 SIO2(A,PT)        -.984     2.867      .157      .157    -3.851     -3.910
7028100 STRENGITE        -2.843    26.318    24.041    26.153   -29.161      2.030
```

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This information defines the aqueous speciation. The following information is then printed for Types III, IV, V and VI species.

- molality
- log K (modified only for temperature)
- DH (enthalpy of reaction)

The molality of a Type III species can be interpreted in different ways depending upon which category it is in. There are four basic categories: redox reactions, components at a fixed activity, solid phases and gases at a fixed partial pressure. The molality of solids and gases has a straightforward interpretation. A positive molality indicates the mass of the solid or gas which precipitated, or was removed, from solution. A negative molality indicates how much mass dissolved or was added to solution. The molality of redox reactions or components at a fixed activity has the same computational meaning but generally lacks any intuitive interpretation, since a redox reaction cannot have any physical mass.

The molality of a Type IV species corresponds to the amount of the solid phase present, or precipitated. Type IV species cannot have a negative mass.

The molality of a Type V species corresponds to the saturation index for that solid.

The molality of a Type VI species can also have a different interpretation depending upon how the reaction is written. For solid phases the molality is the saturation index for the solid. The molality of a Type VI aqueous species is actually the activity of the species. The activity may not be the same activity which would be computed if the species were a Type II aqueous complex since Type VI species are not included in the mass balance equations. For gases the molality represents the computed partial pressure. The molality of Type VI redox reactions generally lacks any intuitive meaning.

Percentage distribution of components--In this section all species are printed which comprise greater than one percent of the total analytical mass for each component. Unfortunately, the percentage distribution may be meaningless for components which appear on both the right and left side of mass action expressions such as H^+ and H_2O.

Saturation indices for Type 6 solids--The following information is printed in this section:

- SI (saturation index)
- log K
- minimum log K

Information is printed for all solids in the data base which have all reaction components present in the input data. The saturation index has been defined under background information (Section 4). A positive log saturation index indicates the solid is oversaturated and a negative log SI indicates the solid is undersaturated. A value of zero indicates equilibrium with the solid. The log SI may not be exactly zero even when the solid is in equilibrium. The problem is to determine the appropriate error band about zero within which equilibrium with the solid is indicated. The error band for a solid should be evaluated on a case by case basis since errors in analytical data or aqueous speciation vary from one water body to another. As a general rule of thumb any log SI within 0.05 times the log K for that solid should be considered as a potential equilibrium phase (Jenne et al. 1980). However this rule causes the error band to vary depending upon which species are chosen as the components and upon the number of components in the solid. Care must be exercised in applying this general rule to all solids because the error band for solids with large numbers of components can sometimes be as large as three or four log units. Another useful guideline is to compute saturation indices using the minimum and maximum log K values, if available. These values are readily computed from Equation (35).

$$\log SI_{max} = \text{maximum} \log K + \log IAP \qquad (35)$$

The computed log SI_{max} and log SI_{min} can give a good idea of the variability in log SI values that could result from errors in the thermodynamic data for solids.

Section 6--

This section computes and prints a charge balance following aqueous speciation. This charge balance is more reliable than the initial charge balance since an aqueous speciation has already been calculated. If the percent difference between cations and anions is greater than 30 percent then an important component was probably not analyzed and the calculations could have significant error.

The total aqueous and adsorbed masses for each component are also printed. The interpretation of this section is straight forward except when the component is a Type III species. In such cases the mass of the Type III species itself, for example H^+ ion, is not included in the aqueous mass. Also the aqueous mass will occasionally be negative for species written on both the left and right sides of the mass action expressions, for example H^+

or H_2O, in such case the aqueous mass is intuitively meaningless. Example output for this section is given in Table 17.

MINTEQ Error Messages

This section describes the printed error messages, their meaning, and appropriate responses.

ERROR (1). "COMPONENTS > NXDIM."

The number of components in the sample data file is greater than the dimensioned array size. The total number of components specified plus any components that MINTEQ inserts, such as H_2O, must be less than 30. Correct this condition by decreasing the number of components. One recommendation would be to eliminate components such as I^-, Cs^+ or Li^+ which do not form strong aqueous complexes. Another option is to eliminate redox reactions, and the appropriate components, in cases where one oxidation state is an unimportant part of the elemental chemistry such as U+3 under oxidizing conditions. If this error occurs repeatedly the X, Y, Z, IDX and GX arrays along with the A matrix should be redimensioned which will require modifying the program.

ERROR (2). "SPECIES > NYDIM".

The total number of species considered in the equilibrium problem exceeds 400. The most likely cause is the consideration of all the solids in the data base as possible equilibrium solids. In such cases the number of Type V species must be reduced. Select the input option that only allows

TABLE 17. SECTION SIX OF THE MINTEQ OUTPUT

```
EXAMS COMPARTMENT NO.  0

 IDX        NAME         AQUEOUS MASS  SORBED MASS      PRECIPITATED MASS
   500   NA                5,220E-04       0,000E-01         0,000E-01
   100   BA                7,282E-07       0,000E-01         0,000E-01
   410   K                 3,581E-05       0,000E-01         0,000E-01
   150   CA                3,044E-04       0,000E-01         0,000E-01
   460   MG                3,085E-04       0,000E-01         0,000E-01
   770   H4SIO4            1.417E-04       0,000E-01         0,000E-01
    20   AG                9,272E-07       0,000E-01         0,000E-01
   180   CL                2,793E-04       0,000E-01         0,000E-01
   732   SO4               8,016E-05       0,000E-01         0,000E-01
    90   H3BO3             4.626E-06       0,000E-01         0,000E-01
   270   F                 5,264E-06       0,000E-01         0,000E-01
   580   PO4               2,211E-06       0,000E-01         0,000E-01
   492   NO3               1,448E-05       0,000E-01         0,000E-01
   490   NH4               7,984E-06       0,000E-01         0,000E-01
   280   FE+2              2,686E-07       0,000E-01         0,000E-01
   281   FE+3              1,254E-08       0,000E-01         0,000E-01
    30   AL                1,853E-07       0,000E-01         0,000E-01
   950   ZN                1,530E-06       0,000E-01         0,000E-01
   160   CD                1,664E-16       8,898E-07         0,000E-01
   600   PB                4,827E-07       0,000E-01         0,000E-01
   231   CU+2              1,574E-06       0,000E-01         0,000E-01
   540   NI                1,703E-06       0,000E-01         0,000E-01
   140   CO3               7,277E-04       0,000E-01         0,000E-01
   330   H                 7,378E-04       0,000E-01         0,000E-01
     1   E                 0,000E-01       0,000E-01         0,000E-01


   2   H2O               4.179E-06       0,000E-01         0.000E-01

    CHARGE BALANCE: SPECIATED

         SUM OF CATIONS =  1,780E-03 SUM OF ANIONS   1,158E-03

         PERCENT DIFFERENCE =   2,117E+01   (ANIONS - CATIONS)/(ANIONS + CATIONS)

    NONCARBONATE ALKALINITY =   2,904E-06

IONIC STRENGTH = :  2,154E-03
```

consideration of a list of designated solids. Then only include the solids which have relatively rapid kinetics of precipitation as Type V. If the number of Type V solids has already been reduced in this manner then the only way to reduce the number of species is to reduce the number of components. This procedure is described under ERROR 1. Changing a species type to VI (species not considered) will not reduce the number of species since the data for these species is also stored in memory.

ERROR (3). "SPECIES NOT FOUND".

This message is preceded by a listing of species not in the data base. The condition is caused by trying to change the type of a species which is not in the data base. This is usually a result of entering the wrong I.D. number for a species, incorrectly formatting the input file or neglecting to include a component. Recheck the species I.D. number and if using batch input check the format field specifications given in Appendix C.

ERROR (4). "CHARGE BALANCE > 30%".

This message indicates that the difference between the summation of charge for cations and anions in the initial solution is greater than 30%. This condition is usually caused by poor water analyses or neglecting to analyze an important component. Water analysis data should be rechecked to insure a component was not neglected. Since this condition is checked prior to speciation, the charge balance at convergence could be acceptable. This usually occurs when such species like CO_3^{2-} are dominant anions. Since total inorganic carbon is entered as CO_3^{2-} all the total carbon is assigned a charge of -2. After speciation, all total inorganic carbon may actually exist as as HCO_3^- with a charge of -1. This in effect creates a computational excess of anions even though the charge balance in the water sample may actually be within the acceptable limits. In such cases, run MINTEQ without considering the charge balance criteria. After the program has finished recheck the final charge balance. If the final charge balance is still greater than 30% the computations could have significant error.

ERROR (5). "INPUT TYPE > SIX".

A species type has been specified in the sample data file which is greater than six. This condition is almost always caused by an error in the sample input format. Check the format fields for inserted species and species with type changes, Appendix C.

ERROR (6). "PHASE RULE VIOLATION".

MINTEQ computationally eliminates a component for every Type III or Type IV species. If MINTEQ tries to equilibrate the solution with a solid phase for which all of the components in the solid dissolution reactions are already fixed, then the phase rule has been computationally violated. An example will make this clearer. Suppose solid quartz is already in equilibrium with the solution, Equation (36).

$$H_4SiO_4 \quad 2\ H_2O + SiO_2\ \text{(quartz)} \tag{36}$$

This means that all of the components in Equation (36) are computationally fixed. H_2O is fixed by the activity of water expression and the activity of H_4SiO_4 is fixed by the dissolution of quartz. Now suppose the model also tries to simultaneously equilibrate the solution with chalcedony, Equation (37).

$$H_4SiO_4 \rightleftharpoons 2\ H_2O + SiO_2\ \text{(chalcedony)} \qquad (37)$$

A phase rule violation will occur because all of the components in the chalcedony dissolution reaction are already fixed. To correct the problem a different list of Type III or IV solids must be entered or one of the solids the model has "selected", usually the last one selected, should be made Type VI.

ERROR (7). "ITERATIONS >ITMAX."

The maximum number of iterations has been exceeded. This condition may occur for a variety of reasons which can generally be grouped into two major categories. The first category is true nonconvergence. The second category occurs when the model is approaching an answer but the computations are terminated by the arbitrary selection of the maximum allowable iterations. The second condition usually occurs as a result of the solid selection process trying to equilibrate the solution with several solids or as a result of extremely poor starting estimates for the component activities. In the latter case the iteration will usually converge if the final computed activities are entered as the initial guesses and the problem restarted. In the case of several solids selected during the solid selection process, merely increase the maximum allowable iterations by selecting the 100 or 200 iteration option in the input. In the case of true nonconvergence the problem is considerably more difficult. In such cases the first suggestion is to enter low starting guesses for the activities of the nonconverging components. This can prevent extremely high masses of individual species occurring in intermediate iterations and thereby causing the activity coefficients to be reset to one. In other words convergence is generally easier if you approach convergence from low component activities. This is particularly true in the case of iron and uranium. Another common problem occurs when the iterative scheme oscillates between two values. Such problems frequently occur when polynuclear species are a dominant part of the total mass. Though these problems are difficult to solve, entering an intermediate activity for the nonconverging components and using the Newton-Raphson plus line search numerical method may enhance convergence.

ERROR (8). "SINGULAR Z MATRIX".

A column in the Jacobian matrix has gone to zero. This condition could happen if the problem is incorrectly defined. For example, setting the total mass of a component to zero without adjusting the component species type, such as setting the mass of Fe^{3+} to zero and not including a redox reaction between Fe^{2+} and Fe^{3+} would cause this error.

ERROR (9). "INVALID COMPONENT".

A component ID number was entered which is not included in the list of acceptable components stored in the component file (LUN3). Recheck the input sample file to make sure all species ID numbers are correct and are in the correct format fields.

ERROR (10). "NOT ENOUGH ADS PARAM".

Insufficient adsorption data were entered. This condition only occurs when using the constant capacitance or triple layer models. The constant capacitance model requires:

- solid concentration
- specific surface area
- inner layer capacitance

The triple layer model requires all of these parameters plus an outer layer capacitance. Recheck the sample description file to insure all necessary information has been entered.

ERROR (11). "A COMPONENT X = 0.0".

The activity of a component has gone to zero. Generally, this cannot happen unless the problem is incorrectly defined. For example, setting the mass of Fe^{3+} to zero and not including a redox reaction between Fe^{2+} and Fe^{3+} can cause this error. This error can also occur in computers where the largest exponent the machine can handle is <40. In such cases, the component can usually be ignored because the activity is very small (i.e., $<1.0 \times 10^{-40}$), and the solution can be modeled without the component present.

ERROR (12). "AN X APPROACHES ZERO."

The activity of a component is almost zero. The cause and solution are described in ERROR(11).

SECTION 7

PROGRAMMERS SUPPLEMENT

This section provides the user with information on the structure of MEXAMS and its three components: MINTEQ, EXAMS and MISP. Each of the subroutines in MINTEQ and MISP are discussed; the reader is referred to the EXAMS user manual and documentation report for a discussion of each EXAMS subroutine. This section also provides details on the modifications made to the EXAMS code, procedures for the implementation of MEXAMS and a discussion of resource requirements.

SYSTEM OVERVIEW

MEXAMS consists of three separate programs. One is a geochemical model (MINTEQ), one is an aquatic exposure assessment model (EXAMS), and the other is a user interactive program that links the two models. All three programs are written in FORTRAN, and are operational on a PDP 11/70 computer system. MINTEQ is also operational on a VAX/VMS 780. However, the VAX version can only be run in the batch mode. Due to their size, both MINTEQ and MISP had to be overlayed prior to implementation on the PDP 11/70. A direct access file was also needed to store some of the larger arrays.

MEXAMS STRUCTURE

Figure 1 (see Section 5, Description of MEXAMS) shows the overall structure of MEXAMS. The detailed structure of the individual components, MINTEQ, EXAMS and MISP are shown in Figures 2, 3 and 4, respectively.

MEXAMS can be used in one of three modes: MINTEQ only, EXAMS only or MINTEQ coupled with EXAMS.

EXAMS Only Mode

In the EXAMS only mode MISP transfers the EXAMS input data to the EXAMS input file FOR005.DAT and EXAMS is initiated with a CALL SPAWN command.

MINTEQ Only Mode

MISP calls subroutine MININ1 to query the user for input data for MINTEQ. If a MINTEQ input file is already available the program will ask for the file name. If an input file is not available subroutines MININ1 and MININ2 will create the file. The procedures for entering data are discussed in detail in Section 6, Guidelines for Use. If the user elects to model the data, MISP initiates MINTEQ through a CALL SPAWN command, and sends the data array IDATA to MINTEQ. IDATA contains flags to let MINTEQ know whether or not a transport model run will be performed. As soon as MINTEQ receives the data array, MISP will become inactive (blocked) while waiting for an event flag to be transferred back from MINTEQ. The command for making MISP inactive is CALL WAITFR (35).

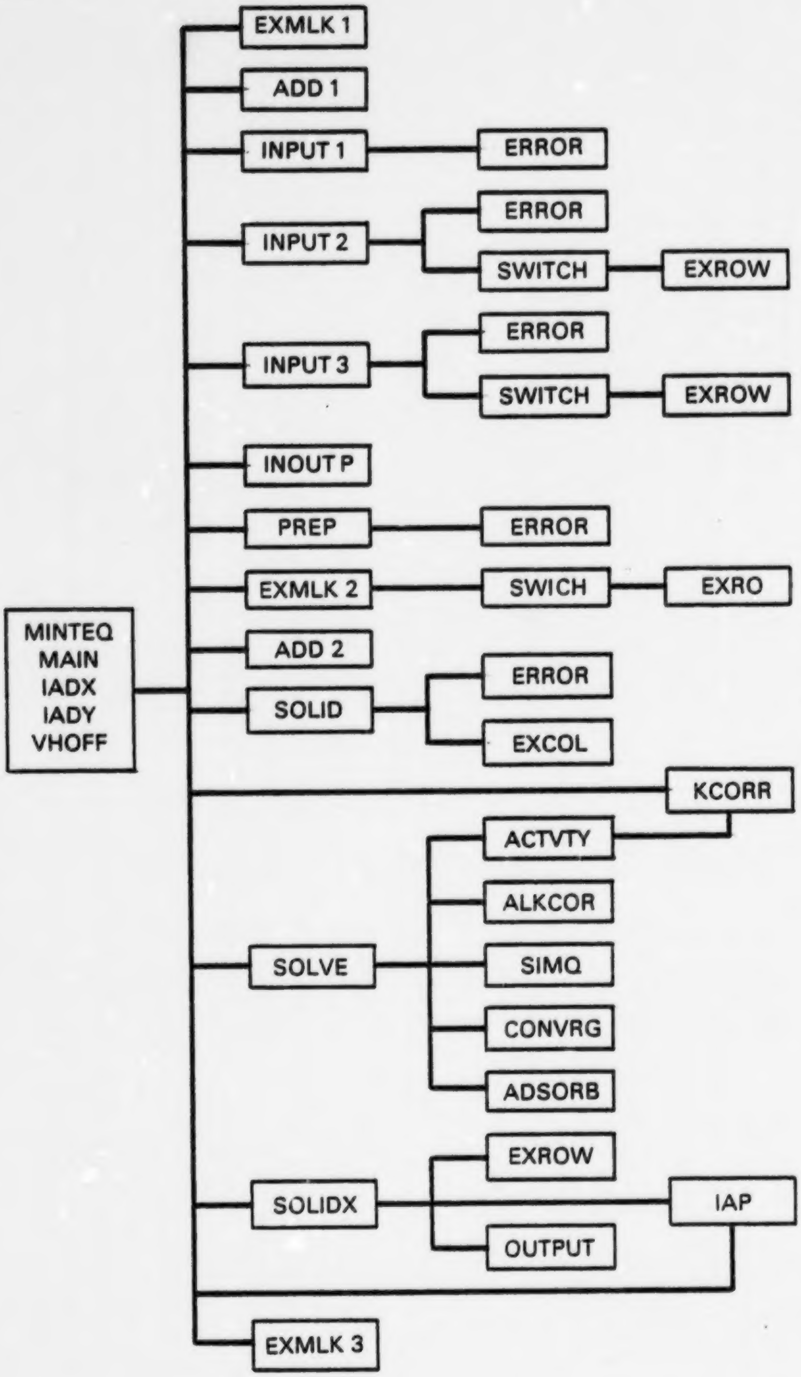
EXMLK 1
ADD 1
INPUT 1
ERROR
INPUT 2
ERROR
SWITCH
EXROW
INPUT 3
ERROR
SWITCH
EXROW
INOUT P
PREP
ERROR
EXMLK 2
SWICH
EXRO
MINTEQ
MAIN
IADX
IADY
VHOFF
ADD 2
SOLID
ERROR
EXCOL
KCORR
ACTVTY
ALKCOR
SOLVE
SIMQ
CONVRG
ADSORB
EXROW
SOLIDX
IAP
OUTPUT
EXMLK 3

Figure 2. Detailed block diagram for MINTEQ.

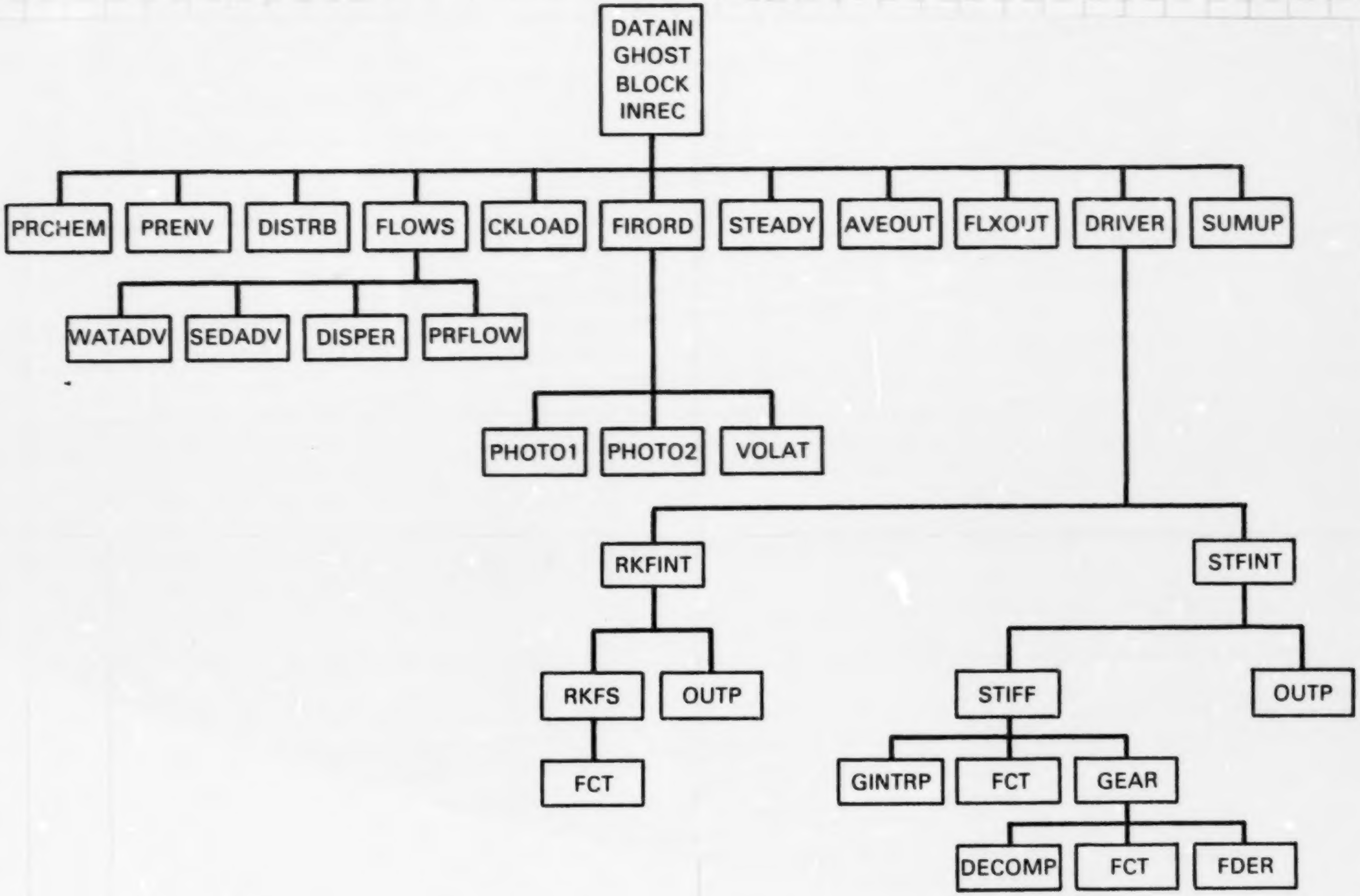
DATAIN
GHOST
BLOCK
INREC
PRCHEM
PRENV
DISTRB
FLOWS
CKLOAD
FIRORD
STEADY
AVEOUT
FLXOUT
DRIVER
SUMUP
WATADV
SEDADV
DISPER
PRFLOW
PHOTO1
PHOTO2
VOLAT
RKFINT
STFINT
RKFS
OUTP
STIFF
OUTP
FCT
GINTRP
FCT
GEAR
DECOMP
FCT
FDER

Figure 3. Detailed block diagram for the batch version of EXAMS (taken from the EXAMS users manual and system documentation report).

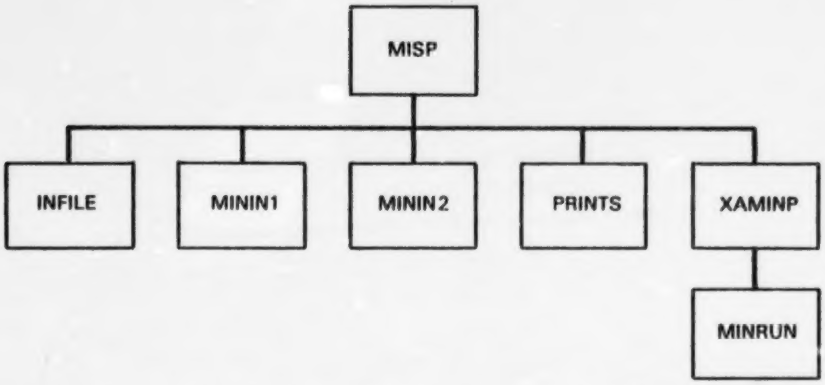

Figure 4. Detailed block diagram for MISP.

MINTEQ will now open its sample data file and read in run specific information through subroutines INPUT1, INPUT2 and INPUT3. Subroutine INOUTP prints out the input data. Necessary preliminary calculations are performed in subroutine PREP. The equilibrium problem is solved by calling subroutines SOLID, KCORR, SOLVE and SOLIDX successively. After the equilibrium problem is solved, three entry points in subroutine OUTPUT are called: OUTCMP, OUTSPC and OUTPC. OUTCMP prints the component information. OUTSPC prints the information for all species types and OUTPC prints the percentage distribution of components. Finally, subroutine IAP is called to compute the saturation indices for all Type VI solids.

Once the geochemical simulation is completed, MINTEQ sets the event flag and stops. This is accomplished through the CALL SETEF (35) command. At this point, MISP becomes active again. This completes a single MINTEQ run.

MINTEQ Coupled with EXAMS Mode

MISP calls subroutine INFILE to query the user about MINTEQ input files and the number of times metals concentrations will be updated with MINTEQ. MININ1 creates the MINTEQ input file MINTEQ.INP. When both EXAMS and MINTEQ input files are ready and closed, MISP subroutine XAMINP initiates EXAMS through a CALL SPAWN command and calls XAMINP, waits for EXAMS to return, processes EXAMS predicted metal, sediment and biomass concentrations to send to MINTEQ, and calls subroutine MINRUN. MINRUN initiates MINTEQ through a CALL SPAWN command and begins accumulating MINTEQ simulation results for EXAMS. The MINRUN-MINTEQ interaction continues until all of the EXAMS metal results have been updated, then MINRUN returns to XAMINP. XAMINP send EXAMS the accumulated results from MINTEQ. The EXAMS-MINTEQ processs continues for as many times as the user initially requested. Then EXAMS finishes the run, sends a flag to XAMINP signalling the end of the run, and stops. MINRUN sends MINTEQ a flag signalling the end of the run, and MINTEQ stops. Then MISP stops.

DESCRIPTION OF MEXAMS ROUTINES

The following provides a detailed description of each of the subroutines in MISP and MINTEQ. The user is referred to the EXAMS users manual and system documentation report for a similar description of EXAMS subroutines. Many of the variable and subroutine names in MINTEQ were retained from either WATEQ3 or MINEQL to assist users of these codes.

MISP Subroutines

MISP queries the user for the simulation mode to be used (MINTEQ only, EXAMS only or EXAMS-MINTEQ). If MINTEQ only is selected, MISP calls subroutine MININ1 and then invokes MINTEQ. If EXAMS only is selected MISP invokes EXAMS. If EXAMS-MINTEQ is selected, MISP calls subroutines INFILE, MININ1, invokes EXAMS, and then calls XAMINP.

Subroutines MININ1 and MININ2--

Subroutines MININ1 and MININ2 displays questions on the user's terminal, processes the user's answers and create an input file for MINTEQ.

Subroutine MINRUN--

Subroutine MINRUN controls the MINTEQ-MISP interactions and manipulates the data being passed to MINTEQ. The inter-program file PASS.DAT is used between MISP and MINTEQ.

Subroutine INFILE--

Subroutine INFILE queries the user for the MINTEQ input file(s) and the number of EXAMS-MINTEQ interactions.

Subroutine XAMINP--

Subroutine XAMINP controls the EXAMS-MISP interactions and manipulates the data returned from EXAMS. The inter-program file TRANSF.DAT is used between MISP and EXAMS.

MINTEQ Subroutines

This section contains a detailed description of the MINTEQ subroutines. A description of the important variables and arrays used in MINTEQ is given in Table 18. A listing of the program is given in Appendix A.

Subroutine ACTVTY--

Subroutine ACTVTY computes all activity coefficients and corrects the equilibrium constants by calling subroutine KCORR.

The first section of the subroutine computes the concentration of aqueous complexes using the activities just computed on a given iteration and the equilibrium constants from the previous iteration. This gives improved values for the ionic strength used in computing activity coefficients. The loop on 100 computes the ionic strength.

If the computed ionic strength exceeds 4.0 molal, the next section of the subroutine sets the ionic strength to an initial starting estimate(a) to prevent large fluctuations in the activity coefficients at intermediate iterations. The loop on 110 computes activity coefficients using the Davies equation. The loop on 150 initializes all activity coefficients for neutral species to 0.1 times the ionic strength. The loop on 120 computes activity coefficients using the extended Debye-Huckel equation for all species with non-zero ion size parameters. If the debug option has been set to one, the values of the IDX, X, IDY, GAMMA, C and Y arrays are printed at each iteration.

(a) The initial starting estimate is simply one half the sum of the analytical molality times the charge squared for all components.

TABLE 18. DESCRIPTION OF IMPORTANT VARIABLES AND ARRAYS USED IN MINTEQ

Parameters	
NXDIM	Dimension of the X arrays
NYDIM	Dimension of the Y arrays
ITMAX	Maximum number of iterations allowed; this value can be adjusted in input
ITER	Iteration counter
EPS	Convergence criteria
NNN	The number of components
TEMP	Water temperature in degrees Celcius
FLAG	Units of input
TEMPK	Temperature in degrees Kelvin
R	Ideal gas constant
VHC	Conversion factor for $\log_{10}$-Naperian log
VH	Van't Hoff correction term
CORALK	Alkalinity input option
IDEBUG	Debug printing option
KOUNT	The number of inserted species or species with type changes not in main memory
AA	Debye-Huckel A parameter
BB	Debye-Huckel B parameter
DENS	Density of water
MU	Computed ionic strength
MUHALF	Square root of MU
NONCRB	Noncarbonate alkalinity
MAXSIZ	Parameter to contol the maximum word size
ICHARG	Input parameter to allow skipping charge balance criteria
LUN0	Logical unit number for output file
LUN1	Logical unit number for input sample file
LUN2	Logical unit number for thermodynamic data file for default species types (2-6)
LUN3	Logical unit number for component data file
LUN4	Logical unit number for type 6 solids file
LUN5	Logical unit number for noncarbonate alkalinity file
LUN6	Logical unit number for the file containing the coefficients of the temperature dependence of log K with temperature.

TABLE 18. (contd)

	Arrays
GX	Log of the component activity
X	Activity of component
T	Total analytical concentration
Y	Value of the difference function
Z	Jacobian matrix
C	Species concentration
GC	Log of species concentration
GK	Log of the equilibrium constant
A	Stoichiometry matrix
IDX	Component I.D. numbers
IDY	Species I.D. numbers
SPCZ	Species Charge
DHA	Debye Huckel ion size parameters
DHB	Debye Huckel ion size parameters
GFW	Specie gram formula weight
DH	Enthalpy of reaction ($\%H^{o}_{r,298}$)
IDYDUM	ID numbers of inserted species or species with type changes which are not in file LUN2
MINGK	Minimum value of the equilibrium constant
MAXGK	Maximum value of the equilibrium constant
NAME	Alphanumeric name of the species
NN	The number of species types one through six
GAMMA	Log_{10} of the species activity coefficient
ALKFCT	Carbonate alkalinity factor

Subroutine ADD--

Subroutine ADD initializes all variables and arrays. The subroutine was pulled out of subroutine MAIN to allow MINTEQ to be overlayed on the PDP 11/70. Subroutine ADD is included in subroutine MAIN in the VAX version of MINTEQ.

Subroutine ADSORB--

Subroutine ADSORB consists of three entry points ADSID, ADINIT, and ADSJAC. All three entry points are called from subroutine SOLVE.

Subroutine ADSORB is only used if the constant capacitance model or triple layer site binding model are used.

Entry ADSID initializes some useful adsorption constants and locates the column numbers for adsorption components. Entry ADINIT computes the potential and the total charge at the various planes from the capacitances and potentials. Entry ADSJAC modifies the Jacobian matrix as described in the MINTEQ technical report.

Subroutine ALKCOR--

This subroutine converts the input value of the alkalinity measured in terms of equivalents into a mass of total inorganic carbon expressed as the molality of CO_3^{2-}.

The loop on 10 computes the excess equivalents of H^+ ion consumed by one

mole of a carbonate containing species over the stoichiometry of carbonate in the species. The loop on 200 reads the noncarbonate alkalinity file on the first iteration only. The loop on 400 sums the equivalents of noncarbonate alkalinity. The next section computes the mass of carbonate. If the computed mass of carbonate is negative the mass is set to the input alkalinity times two. There are debug prints in both the carbonate and noncarbonate alkalinity routines.

Subroutine CONVRG--

Subroutine CONVRG modifies the Newton-Raphson corretion terms using a modified line search technique. The subroutine uses past iteration points to help predict new values of the unknown activities. The purpose of the line search is to estimate values of the unknowns that are close enough to the true answer to allow Newton-Raphson to converge. When the mass balance criteria are satisfied within 50%, the line search is stopped. The data points for the current and previous iterations are stored in the P matrix. The method is described in detail in the MINTEQ technical document.

Subroutine ERROR and ERROR2--

Subroutine ERROR is called only when a fatal error occurs in the program. An error message is written to LUNO, followed by component and other species information for the current iteration. Then MINTEQ stops execution. Subroutine ERROR2 was added only to facilitate the PDP 11/70 overlay.

Subroutine EXCOL--

This subroutine merely exchange the columns JO and JJ passed from subroutine SOLID. Columns JO and JJ of the IDX, X, GX and T arrays are exchanged along with the corresponding columns of the A matrix.

Subroutines EXROW and EXRO--

These subroutines exchanges rows IO and II passed from subroutines INPUT, SOLIDX or SWITCH. Rows IO and II are exchanged in the following arrays: IDY, C, GK, DHA, DHB, GFW, SPCZ, DH, NAME, MINGK, MAXGK, and GAMMA. Rows IO and II are also exchanged in the A matrix. Subroutine EXRO was added only to facilitate the PDP 11/70 overlay and is not included on the VAX version.

Subroutine EXMLK--

This subroutine reads and writes data to file PASS.DAT which is also accessed by MISP. The subroutine has three external entry points, EXMLK1, EXMLK2, and EXMLK3.

EXMLK1 reads the input file PASS.DAT if MISP is in the MINTEQ-EXAMS mode. The following information is read from PASS.DAT.

- MINTEQ output option for this compartment (IOUT),
- The component ID for the metal being followed (ICIDX),
- The aqueous plus adsorbed mass of metal (AQMASS),
- The sediment concentration in mg/ℓ (SEDCON),
- The concentration of biota in mg/ℓ (BIOCON),
- The number of precipitated solids (IPRCPT),
- The ID number for each solid (IPIDY) and the mass of each solid in moles/ℓ (PRECIP).

EXMLK2 initializes the appropriate arrays with the information read in EXMLK1.

EXMLK3 computes the necessary information to pass back to MISP. The following data is written to file PASS.DAT.

- The total mass of metal adsorbed onto biota (BV),
- The total mass of metal adsorbed on sediments (SV),
- The dissolved concentration of metal (V),
- The ID number for each precipitated solid (IDY),

- The mass of each precipitated solid (C),
- Conversion factor for each solid from moles/ℓ to mg/ℓ (CF).

Functions IADX and IADY--

Function IADX finds the column number for component IDXT. Function IADY finds the row number for species IDYT.

Subroutine IAP--

Subroutine IAP computes the saturation indices for all solids in the Type VI solids file. The loop on 120 computes the ion activity products and the saturation indices. The loop on 130 checks to insure inserted species (see Appendix C) were not Type VI solids. If an inserted species has the same ID number as a Type VI solid then two asterisks are printed immediately before the data for that solid to indicate the inserted species is already in the data base.

Subroutine INOUTP--

Subroutine INOUTP is called from MAIN immediately after SUBROUTINE INPUT3. INOUTP prints the initial input data for all species types. This subroutine is included in subroutine OUTPUT on the VAX version of MINTEQ.

Subroutine INPUT1--

Subroutine INPUT1 reads the run specific information needed to set up the equilibrium problem. The sample description file (LUN1) is read first.

Beginning with preliminary information, such as sample description, temperature and various program options. The Van't Hoff correction term is set equal to:

$$VH = (298.16 - TEMPK)/(298.16 \times TEMPK \times VHC \times R) \quad . \qquad (38)$$

Van't Hoff temperature correction of Equilibrium constants is explained in the MINTEQ technical document. The loop on 10 brings in the component information. The next section inserts the H20 and dissolved sulfur S(0) components. S(0) is only inserted if component HS is included and the user does not have analytical data for S(0). The loop on 205 insures all components are valid. Once the component is found in file LUN3 the loop on 200 fills out the appropriate arrays.

Subroutine INPUT2--

Subroutine INPUT2 reads thermodynamic data for species Types II through VI from file LUN2. The Type VI species in this file are not solids. The loop on 400 sets the species types. The loop on 340 inputs the thermodynamic data and the loop on 300 checks to see if all of the components for that species are present before the data are stored in memory.

The next block of code reads species modifications and type changes from file LUN1. A search is begun to find the species and the previous species type. When the species is found, a call to subroutine SWITCH changes species types. The loop on 710 searches memory. If the species is not found in memory the necessary information is stored in local arrays until all type changes have been read from file LUN1. The Type VI solids file is then searched for the species not found in memory. If these species are not found in the Type VI solids file, an error message is printed and the program terminates.

Subroutine INPUT3--

Subroutine INPUT3 allows insertion of species not in the thermodynamic data base. The loop on 990 performs the species inserts. The loop on 993 checks to insure all of the components for the inserted species are in memory. The loop on 600 searches main memory to insure the species is not already in the data base. If the species is found in memory, a message is printed and the species is ignored. Otherwise the ID number is stored in array IDYDUM which will be checked in subroutine IAP to insure the inserted species was not a Type VI solid. Subroutines INPUT1, INPUT2, and INPUT3 are combined in subroutine INPUT in the VAX version of MINTEQ.

The next section of code changes S(0) and H_2O to Type III species if S(0) was not an analytical input.

Subroutine KCORR--

Subroutine KCORR modifies the equilibrium constants for ionic strength for Types I and II species. The equilibrium constants are modified by,

$$\log K_i = \log K_i - \log \gamma_i \quad (39)$$

where γ_i is the activity coefficient for species i and K_i is the equilibrium constant for species i. Since the ionic strength may vary during the iterative procedure, the log K_i in Equation (39) must be reset to the values at infinite dilution every iteration. This is done in the loop on 200. The entry KCORR2 is called from subroutine MAIN to reset the infinite dilution log K_i terms every time the log K_i terms are modified for solids. Debug option 3 in KCORR2 prints the values for NNN, NN(1), NN(2), and the IDY,GK and GK1 arrays.

Subroutine OUTPUT--

Subroutine OUTPUT has three entry points. These entry points are OUTCMP, OUTSPC and OUTPC. They are called from various subroutines. OUTCMP prints component data for such parameters as activity, concentration, and the activity coefficients during the iterative process. This entry is called from subroutines ERROR and SOLIDX and from the MAIN program. Entry OUTSPC prints information for all species at various times during the SOLID-SOLIDX loop in MAIN. The output information is different for the various species types. The different output was selected to minimize confusion to the user. OUTPC performs several functions. The loop on 110 calculates and prints the percentage distribution of components. All species which comprise greater than 1% of the analytical mass of the component are printed. If a different tolerance is desired reset THRSH in subroutine MAIN. The loop on 180 computes the aqueous and adsorbed masses. For this routine to work the ID numbers for sorbed species must be greater than 9900000. The mass of Type III aqueous species such as H^+ ion are not included in the computed aqueous mass. The loops on 200 and 230 compute the final charge balance. The loop on 900 prints the values of the IDX, IDY, X, C, and Gamma arrays if debug option one is selected.

Subroutine PREP--

Subroutine PREP performs a series of preliminary calculations to setup the equilibrium problem. The loop on 100 corrects all equilibrium constants for temperature using the Van't Hoff relation by calling function VHOFF. The loop on 660 reads in the coefficients for the analytical expressions of log K with temperature. The loop on 680 then modifies the equilibrium constants using the analytical expressions. The analytical expressions for log K with temperature are described in the MINTEQ technical document. The next section of code computes the Debye-Huckel A and B parameters as a function of temperature. This section of code was translated directly from WATEQ2 (Ball et al. 1979) as documented in Truesdell and Jones (1974). The next section of code converts all analytical units to molality. The loop on 150 initializes the X and GX arrays to the total mass divided by 100 for components with no activity guess.

The activity of water is set by modifying the equilibrium constant,

$$GK_{water} = -\log (1.0 - 0.017 \times CC1) \tag{40}$$

where CC1 is the summation of the analytical molality of all components. The loop on 160 computes a cation/anion balance. An error message is generated if the imbalance exceeds 30%. The final part of subroutine PREP prints the IDX, IDY, NAME, X and C arrays if debug option one is selected.

Subroutine SIMQ--

Subroutine SIMQ is identical to subroutine SIMQ in MINEQL. The Jacobian matrix is solved by gaussian elimination and back substitution. The Y array is modified as follows:

$$\overline{Y} = (\bar{x}^{n+1} - \bar{x}^{n}) \tag{41}$$

where n is the iteration number. The new values of the activities at the new iteration (x^{n+1}) are then recomputed in subroutine SOLVE.

Subroutine SOLID--

Subroutine SOLID modifies the T and GK arrays and the A matrix for the presence of Type III and IV species. The mathematics is described by Westall et al. (1976). Subroutine SOLID is identical to subroutine SOLID in MINEQL except for the debug print. If debug option four is selected, the values of the IDX, X, IDY, C and GK arrays are printed.

Subroutine SOLIDX--

Subroutine SOLIDX unmodifies the T, X, GX and GK arrays for the presence of solids, computes the amounts of solids and selects the thermodynamically stable solids. The loops on 460 compute the mass of solids and unmodifies the arrays. The mathematics is described by Westall et al. (1976). The loop on 210 computes the saturation indices for Type V and VI species. The loop on 770 is a debug print which is identical to the debug routine in subrountine SOLID.

The next section of code embodies the solid selection routines described in Section 4 of the MINTEQ technical report . Solids are checked first for dissolution, if the mass of any Type IV species is negative the solid is dissolved by switching the species type to V. Control is then passed to subroutine MAIN. If no solids have dissolved the solids are checked for precipitation. If solids are oversaturated then the highest ranked solid is precipitated by switching the species type to IV. The loops on 300 and 320 allow user designated output at various points in the solid selection process.

Subroutine SOLVE--

Subroutine SOLVE solves the chemical equilibrium problem created by SOLID and SOLIDX. The loops on 2 and 3 compute the concentration of all aqueous complexes. Next subroutine ALKCOR is called if alkalinity was input and entry ADINIT is called if the constant capacitance or triple layer adsorption models are being used. The loop on 201 resets the Y array to:

$$Y_j = - T_j + \sum_{i=1}^{m} a(i,j)C_i$$

where Y_j is the difference function for component j, T_j is the analytical mass for component j, m is the number of aqueous species, C_i is the concentration of species i, a(i,j) is the stoichiometry of component j in species i, (see Section 4 of the MINTEQ technical report. The loop on 300 computes the Jacobian matrix. Next, ADSJAC is called to modify the Jacobian if the constant capacitance or triple layer adsorption models are being used. Statement 811 checks for convergence. If the problem has not converged a new iteration is begun. Subroutine SIMQ is called and the difference between the new activities and the old activities is passed back in the Y array. New values for the activities are computed and the equilibrium constants are corrected for ionic strength by calling ACTVTY. When a new iteration is begun the data for the previous iteration is printed.

Subroutines SWITCH and SWICH--

Subroutine SWITCH changes species types. Species I is moved from Type L (the previous type) to LTYPE (the new type). This subroutine was originally part of subroutine INPUT in MINEQL. It was made a separate subroutine because of the number of places it must be accessed in MINTEQ. Subroutine SWICH is identical to subroutine SWITCH. SWICH was created to facilitate the PDP 11/70 overlay.

Function VHOFF--

Function VHOFF corrects the equilibrium constants for temperature by Equation (42),

$$\text{Log } K_T = \log K_{298} - \Delta H^{o}_{r,298} * \text{VH} \tag{42}$$

where VH has been initialized as described in subroutine INPUT, K is the equilibrium constant and ΔH^{o}_{r} is the enthalpy of reaction. Function VHOFF is accessed from subroutines PREP and IAP.

EXAMS CODE MODIFICATIONS

As was discussed in Section 6, Guidelines for Use, several modifications were made to the batch version of EXAMS. None of these modifications affect the use of EXAMS for the analysis of organics. The modified subroutines are shown in Figure 5. They are DATAIN, GHOST, DISTRB, DISPER, FIRORD, AVEOUT, DRIVER, RKFINT, RKFS, STFINT, STIFF, and OUTP. The main changes made to each subroutine are discussed below.

Common PART1L

- Dimension of the variable, ALPHA was changed from ALPHA (18,010) to ALPHA (19,010)

- The new variable, KFLAG, was added to the transfer list from MISP to EXAMS. KFLAG is the number of times MINTEQ will be used to update the "steady-state" computation performed by EXAMS.

- The new variable, LFLAG was added to transfer from MISP to EXAMS the number of times MINTEQ will be used to update the "persistence" computations performed by EXAMS.

- The new variable, LCNT, was added as a timestep counter for the "persistence" computation.

- The new variable KCNT was added as a loop counter for the "steady-state" computation.

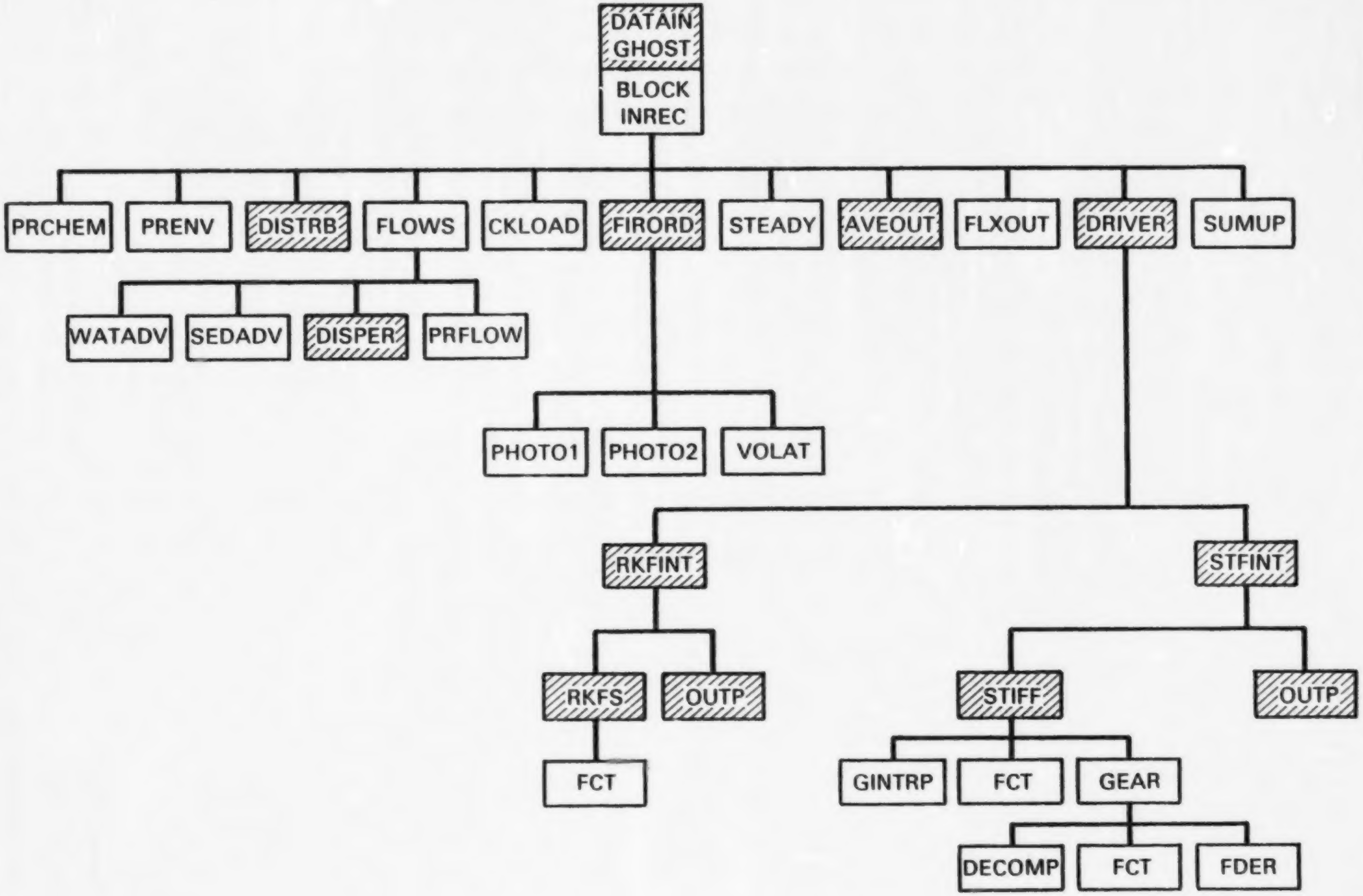
DATAIN
GHOST
BLOCK
INREC
PRCHEM
PRENV
DISTRB
FLOWS
CKLOAD
FIRORD
STEADY
AVEOUT
FLXOUT
DRIVER
SUMUP
WATADV
SEDADV
DISPER
PRFLOW
PHOTO1
PHOTO2
VOLAT
RKFINT
STFINT
RKFS
OUTP
STIFF
OUTP
FCT
GINTRP
FCT
GEAR
DECOMP
FCT
FDER

Figure 5. Detailed block diagram for the batch version of EXAMS showing the subroutines that were modified (cross hatched).

Common RESULT

- Dimension of the variable Z was changed from Z(18) to Z(21).

Common RESLT

- Dimensions of the variables DOMAX, MAXPT, DOMIN, MINPT were changed

  from DOMAX(10) to DOMAX(12),
  from MAXPT(10) to MAXPT(12),
  from DOMIN(10) to DOMIN(12),
  from MINPT(10) to MINPT(12).

Subroutine DATAIN

- The variable, KCNT, was initialized to be zero

```
KCNT = 0
```

- The variable, LCNT, was initialized to be zero

```
LCNT = 0
```

- After all the computations are completed in EXAMS or errors in input data are discovered by EXAMS, subroutine DATAIN sends the following signal to inform MISP that the EXAMS simulation has been completed:

```
CALL SETEF(39,IDS)
```

Subroutine GHOST

- Sends a signal to MISP that EXAMS is ready to accept metal concentrations updated by MINTEQ:

```
CALL   SETEF(37,IDS)
CALL   WAITFR (38,IDS)
CALL   CLREF(38,IDS)
```

- Receives KFLAG from MISP. Depending on the value of KFLAG, the following variables for all the compartments will be provided by MISP to EXAMS:

  ALPHA(16,J), ALPHA(17,J), ALPHA(18,J), and ALPHA(19,J),

  where J is the compartment number.

Note that these four values correspond to the fraction of precipitated, dissolved, sediment-sorbed and bio-sorbed metal in each compartment.

This process will be repeated in GHOST until all of the metal fractions required for the steady state computations have been updated by MINTEQ values.

Subroutine DISTRB

- Since the modified EXAMS includes precipitation, the size of the ALPHA array was changed. This change in dimension required some adjustments such as

```
DO   210   I = 17,19
ALPHA(I,J) = 0
K1 = I-16
K2 = I-3
DO   200   K = K1,K2,3
  ALPHA(I,J) = ALPHA(I,J) + ALPHA(K,J)
200 CONTINUE
210 CONTINUE
```

Subroutine DISPER

- Similar to Subroutine DISTRB, the dimension change of the ALPHA array made adjustments to the program necessary.

- The main change in this subroutine was to replace ALPHA(17,J) by ALPHA(16,J) + ALPHA(18,J). This substitution is based on the assumption that the precipitated metal is transported with the sediment in compartment J. This change includes the metal dispersion computation as follows:

```
SEDFL(KK,K3) = SEDFL(KK,K3) + TEMSED
  *[ALPHA(17,K3)*SEDCOL(K3)]/[ALPHA(16,K3) + ALPHA(18,K3)]
  *[ALPHA(16,KK) + ALPHA(18,KK)]/[ALPHA(17,KK)*SEDCOL(KK)]
```

Subroutine FIRORD

- Adjust ALPHA array references to reflect the change in dimensions such as

  TEMP3 = ALPHA(17,J)*100

  instead of

  TEMP3 =ALPHA(16,J)*100

- Change EXPOKL, INTOUL, INTINL and TEMP3 to include both sediment-sorbed and precipitated metals as sediment resident quantities. For example,

```
EXPOKL(J) = WATOUL(J)*ALPHA(17,J) + SEDOUL(J)
  *[ALPHA(16,J) + ALPHA(18,J)]/SEDCOL(J) + WATOUL(J)
  *ALPHA(19,J)*PLRAG(J)
INTOUL(J) = INTOUL(J) + WATFL(I,J)*ALPHA(17,J)
  + SEDFL(I,J)*[ALPHA(16,J) + ALPHA(18,J)]/SEDCOL(J)
  + WATFL(I,J)*ALPHA(19,J)*PLRAG(J)
```

Subroutine AVEOUT

- Adjust ALPHA array references to reflect the change in dimensions.

- Adjust the size of the Z array to accomodate additional precipitated metal concentration values. This leads to many additions and changes, including,

```
Z(2) = Z(2) + ALPHA(18,J)*Y(J)/SEDCOL(J)
Z(20) = Z(20) + ALPHA(16,J)*Y(J)
```

- Add a calculation of the average, maximum and minimum precipitated metal concentrations

- Add the number of total compartments, KOUNT; the sum of computed steady-state dissolved, sediment-sorbed, and biosorbed metal concentrations, SPECON; precipitated metal concentrations, PRECON; sediment concentration, SEDCON(J); and the biomass concentration, BIOCON(J) for all compartments in the file "TRNSF.DAT" in Logical Unit 11. This file will then be read by MISP to supply these concentrations to MINTEQ to update ALPHA values.

Subroutine DRIVER

- Remove equivalence statement with W array.

- Remove variables, KOUNT, TFINAL, TINCR, T, IFLAG and TPRINT from arguments at Subroutines RKFINT and STFINT because these variables are in COMMON storage areas SETUPG and TIMEL which were added to Subroutine RKFINT and STFINT.

Subroutine RKFINT

- Remove varibles KOUNT, TFINAL, TINCR, T, JFLAG and IPRINT from the argument list.

- Include 'GLOBAL.COM', 'CHEML.COM' and 'ENVIRL.COM'.

- Similar to the steady state case performed in Subroutine GHOST, this subroutine sends signals to MISP to receive metal concentrations updated by MINTEQ for the persistence computation. This involves:

  - determining if MISP/MINTEQ must be called or not,
  - sending signals to inform MISP that EXAMS is ready to read data from MISP
  - reading KFLAG and LFLAG. Depending on LFLAG and LCNT, reading ALPHA values for all compartments updated by MINTEQ from MISP through file "TRNSF.DAT" in Logical Unit 11.

    ```
    READ(11,103) [ALPHA(I,J), I=16,19), J=1,KOUNT]
    ```

- After new ALPHA values are read from MISP/MINTEQ, RKFINT updates the INTINL value based on new ALPHA values for all compartments:

```
INTINL(I,J) = WATFL(J,I)*ALPHA(17,I)
  + SEDFL(J,I)*[ALPHA(16,I) + ALPHA(18,I)]/SEDCOL(I)
  + WATFL(J,I)*ALPHA(19,I)*PLRAG(I)/WATVOL(J)
```

- The update of ALPHA and INTINL for the persistence computation will be repeated a number of times preassigned by the user.

- Send signals to MISP and receives updated fractions of dissolved, sediment-sorbed, biosorbed and precipitated metal for the persistence computation.

Subroutine STFINT

- Modifications made in this subroutine are the same as those in Subroutine RKFINT.

Subroutine OUTP

Modifications made in this subroutine are similar to those in Subroutine AVEOUT.

- Adjust ALPHA
- Write KNTDUM,J,ALPHA in file "TRNSF.DAT" in Logical Unit 11 for MISP/MINTEQ to read.
- Send a signal to MISP when the persistence computation is completed.

MINTEQ SUPPORTING DATA FILES

MINTEQ has five supporting data files. The data files are assigned logical unit numbers in the main program.

File LUN1

This file contains a description of the water analyses and other run specific information. File LUN1 is described in detail in Appendix C.

File LUN2 - Default Thermodynamic Data

File LUN2 contains thermodynamic and accessory data for all species types except components and Type VI solids. The data are arranged in such a manner that as they are read into memory a specific type is automatically assigned. The first group of data is for aqueous complexes of Type II. MINTEQ detects the end of Type II species by reading two blank lines. Since there are no default Type III or IV species, the next four lines are blank. The next group of data is for Type V species. It is also terminated with two blank lines. The last group of data is for default Type VI species. The file terminates with two blank lines.

Species types are separated by two blank lines and there are two lines of data for each species. Line one has format (I7, 1X, A12, 2F10.4, 2F8.3, 3F5.2, F9.4) and the format fields correspond to the species ID number, name, enthalpy of reaction, equilibrium constant, minimum equilibrium constant, maximum equilibrium constant, charge, Debye-Hückel A, Debye-Hückel B, and gram formula weight. Line two has format [F 5.2, 1X, I1, 3X, 8(F7.3, 1X, I3, 3X)] and the format fields correspond to the: alkalinity factor, number of components in the reaction, stoichiometry of component n and ID number of component n.

File LUN3 - Component Data File

File LUN3 contains the necessary data for the components. Each component has only one line of data in format (I3, 1X, 2A4, F4.1, 4X, F5.2, 8X, F11.5). The format fields correspond to the ID number, name, charge, Debye-Hückel A, Debye-Hückel B, and the gram formula weight. There must be a blank line at the end of the file. This file must be modified every time a new component is added.

File LUN4 - Type VI Solids File

This file contains the thermodynamic and accessory data for all solid phases in the data base. By storing the solids data in both files LUN2 and LUN4 it is easy to allow the solids to default to either Type V or VI. Also, if the solids default to Type VI, file LUN4 eliminates the need to store all solids data in memory when it will only be needed at the very end of the program.

File LUN4 contains two lines of data for every solid phase. There must be two blank lines at the end of the file to prevent an end of file condition. The format fields for each line of data are identical to file LUN2.

File LUN5 - Noncarbonate Alkalinity

This file contains the noncarbonate alkalinity information. The selected noncarbonate alkalinity species were taken from the WATEQ3 code (Ball et al. 1981). To add or delete species considered in the noncarbonate alkalinity calculations requires modifying this file.

File LUN5 contains one line of data for each species which consists of the species ID number and the noncarbonate alkalinity factor. There must be one blank line at the end of the file. File LUN5 is reproduced in Table 19. The species name is provided only for information and is not included in file LUN5.

File LUN6 - Analytical Expression File

File LUN6 contains the coefficients for the analytical expressions of log K with temperature. The coefficients A through G are for the following generalized expression:

$$\log_{10} K(T) = A + B \cdot T + C/T + D * \log_{10} T + E \cdot T^2 + F/T^2 + G/\sqrt{T} \quad .$$

MINTEQ DATA STORAGE STRUCTURE

The data storage system is very simple. All major arrays are related to the rows or columns of the A (stoichiometry matrix). Information for components is stored in arrays which correspond to the columns of the A

TABLE 19. NONCARBONATE ALKALINITY SPECIES

ID Number	Name	Noncarbonate Alkalinity Factor
0303302	$Al(OH)_4^-$	1.00
3307701	$H_2SiO_4^{2-}$	2.00
3307700	$H_3SiO_4^-$	1.00
3300900	$H_2BO_3^-$	1.00
3305800	HPO_4^{2-}	1.00
3307301	S^{-2}	2.00
3300000	OH^-	1.00
580	PO_4^{3-}	2.00
730	HS^-	1.00

matrix. Information for all species types is stored in arrays which correspond to the rows of the A matrix. Figure 6 presents a schematic visualization. The array names are defined in Table 18.

MINTEQ divides the rows and columns into blocks. The rows are divided into six blocks; one block for each species type. The NN array contains the number of species in each block. The columns are divided into two blocks. The first block contains components with a mass total. The second block contains components with an established fixed activity relationship as a result of modification for the presence of Type III or IV species.

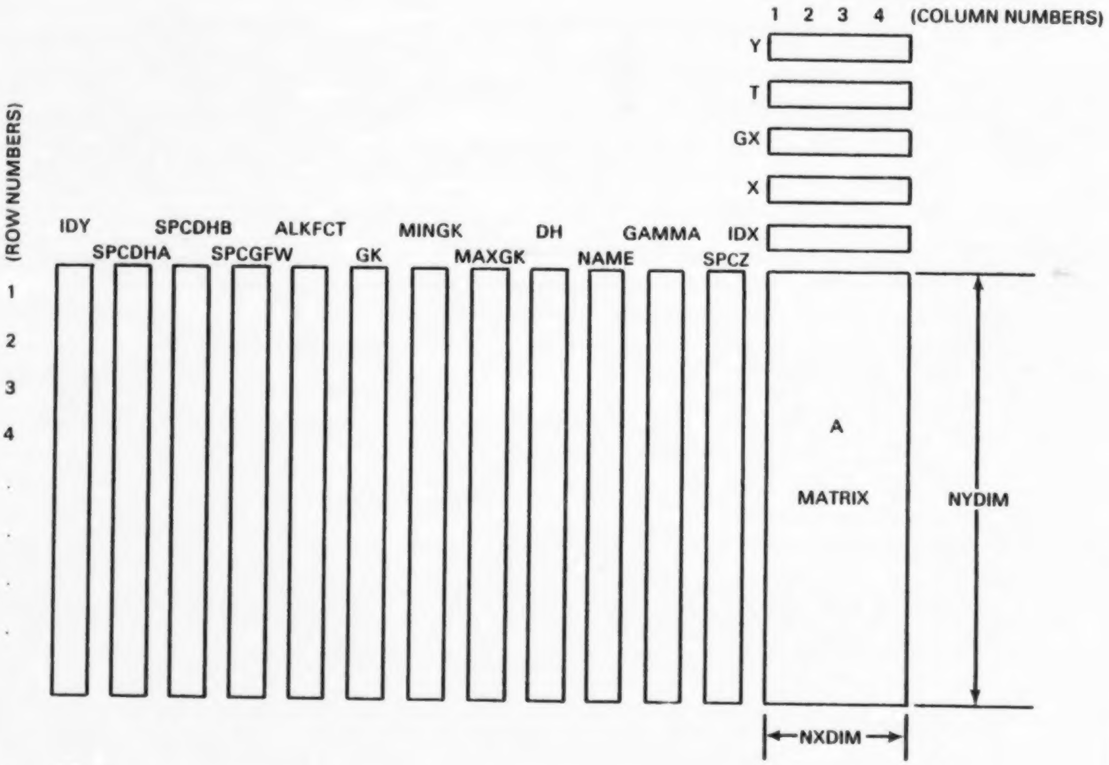
1 2 3 4 (COLUMN NUMBERS)
Y
T
GX
X
IDX
(ROW NUMBERS)
1
2
3
4
IDY
SPCDHA
SPCDHB
SPCGFW
ALKFCT
GK
MINGK
MAXGK
DH
NAME
GAMMA
SPCZ
A
MATRIX
NYDIM
NXDIM

Figure 6. Visualization of data storage structure.

MEXAMS IMPLEMENTATION PROCEDURE

All files needed to implement MEXAMS on a PDP 11/70 will be on a 1600 bpi magnetic tape with a VOLUME-ID of MEXAMS. The standard PDS copy command will be used to put the files on the tape. The following files will be needed:

For MISP:

1. MISPF4P.CMD - for FORTRAN compilation
2. MISPLNK.CMD - to create MISP
3. MISP.FTN - driver program
4. Six subroutines - listed in the discussion entitled DESCRIPTION OF MEXAMS ROUTINES
5. MISP.CMN - MISP common block
6. XAMINP.CMN - common block
7. MININP.CMN - common block
8. MISP.ODL - MISP overlay.

For MINTEQ:

1. MINTEQF4P.CMD - for FORTRAN compilation of 23 MINTEQ routines
2. MINTEQLNK.CMD - to create MINTEQ.TSK
3. MINTEQ.ODL - overlay instructions for MINTEQLNK.CMD
4. MINTEQ.CMN - 'INCLUDE' file with common blocks and TYPE declarations for MINTEQ routines
5. SORBS.CMN - common block for specific MINTEQ routines
6. Twenty three routines - listed in the discussion entitled DESCRIPTION OF MEXAMS ROUTINES.

Five data files for MINTEQ:

1. THERMO.DAT(LUN2) - default thermodynamic data
2. COMP.DAT(LUN3) - component data
3. TYPE6.DAT(LUN4) - thermodynamic data for solid phases
4. ALK.DAT(LUN5) - noncarbonate alkalinity information
5. ANALYT.DAT(LUN6) - analytical expressions of log K with temperature.

For a description of the five data files, see the previous discussion entitled Supporting Data Files. In the PDP 11/70 version files THERMO.DAT and TYPE6.DAT must be binary with file names THERMO.BIN and TYPE6.BIN.

Copy the files to the system disk into one UIC. Then enter the following commands.

```
PDS> @ MISPF4P.CMD
PDS> @ MISPLNK
PDS> @ MINTEQF4P
PDS> @ MINTEQLNK
```

MISP and MINTEQ.TSK are now ready to use. If the files are put on a user's disk, then the command files will require modification to include the disk name.

MINTEQ IMPLEMENTATION TEST CASES

This section describes the results of two example test cases run with MINTEQ. These cases are provided to aid in testing the implementation of MINTEQ on a new computer system.

The first test case is a seawater test case published by Nordstrom et al. (1979). This case is intended primarily as a comparison of the MINTEQ modeling results to those of several other geochemical models compared by Nordstrom et al. (1979) using the same seawater test case.

Only the thirty most important components were selected for comparison. Table 20 presents a comparison of the trace metal speciation computed by MINTEQ and the results for several other geochemical models published in Nordstrom et al. (1979).

Table 20 shows that MINTEQ results compare very closely to WATEQ2. This is expected since the MINTEQ thermodynamic data were taken from WATEQ3 (Ball et al. 1981). The small differences between MINTEQ and WATEQ2 appear to result from small differences in activity coefficients for the major species (see Nordstrom et al. 1979, Table VIII). WATEQ2 uses the Davies equation to compute many of the activity coefficients for major species, whereas MINTEQ uses the extended Debye-Huckel with parameters taken from Table 1 of the WATEQ3 data base (Ball et al. 1981).

A complete listing of the MINTEQ output for the seawater test case is given in Appendix B.

The second test case is a modified form of the river water test case given in Nordstrom et al. 1979. This test case is intended primarily as an example of some MINTEQ features, not as a direct comparison to other models. This test case was modified to show the following features:

- an "activity Kd",
- fixed partial pressure of $CO_2(g)$,
- the input of a list of considered solids,

TABLE 20. A COMPARISON OF SELECTED MINTEQ TRACE METAL SPECIATION WITH THE RESULTS OF SEVERAL GEOCHEMICAL MODELS PUBLISHED IN NORDSTROM ET AL. 1979. ALL VALUES ARE GIVEN AS -LOG MOLALITY

Species	EQ3	GEOCHEM	SOLMNEQ	WATEQF	WATEQ2	MINTEQ
Ba^{2+}	---	6.93	6.857	6.821	6.821	6.810
Mn^{2+}	9.287	9.33	8.478	8.654	8.654	8.617
$MnCl^{+}$	---	10.26	29.376	8.880	8.881	8.936
Fe^{3+}	17.466	22.94	---	17.897	17.897	17.953
$Fe(OH)_3^0$	---	11.28	---	8.071	8.071	8.096
$Fe(OH)_4^-$	7.439	12.41	---	7.664	7.664	7.643
Ni^{2+}	---	9.23	---	---	8.813	8.750
$NiCl_2^0$	---	9.74	---	---	9.335	9.283
$NiCO_3^0$	---	7.91	---	---	7.590	7.582
Cu^{2+}	9.056	11.21	---	---	10.153	10.001
$CuCO_3^0$	---	10.01	---	---	9.070	9.114
Ag^{+}	14.797	16.79	14.477	---	14.394	14.355
$AgCl_4^{3-}$	9.517	12.48	9.617	---	9.684	9.682
Zn^{2+}	7.346	8.35	7.321	---	7.547	7.508
$ZnCO_3^0$	---	7.33	---	---	7.894	8.051
Cd^{2+}	---	11.11	---	---	11.257	10.550
$CdCl^{+}$	---	9.99	---	---	9.371	9.407
$CdCl_2^0$	---	9.94	---	---	9.369	9.443
Pb^{2+}	13.746	11.68	10.442	---	11.335	11.282
$PbCl_2^0$	13.591	11.41	0.372(a)	---	11.017	10.975
$PbCO_3^0$	9.602	16.09	9.743	---	9.743	9.743

(a) Appears to be an error in Nordstrom et al. (1979)

- the process used for solid selection,
- an example of how to insert species not in the data base, and
- computation of pE from Fe(II) and Fe(III) analysis.

The concentration of the trace constituents Zn, Cd, Pb, Cu, Ag, and Ni were set at 100 μg/ℓ. The solid Cerargyrite (AgCl) was found to be supersaturated during the computation. Since Cerargyrite was included as a considered or permissible precipitating solid, MINTEQ precipitated Cerargyrite until the aqueous solution was in equilibrium. Seventy-one percent of the initial silver precipitated as Cerargyrite.

The computed pE from Fe(II) and Fe(III) analysis was 1.39 or an Eh of 0.078 V. This Eh compares poorly with a value obtained by the platinum Eh electrode of 0.440 V, illustrating the discrepancies frequently found between platinum electrode Eh values and Eh values computed from analysis of individual elemental oxidation states.

This test case is particularly useful to users who are just beginning to use MINTEQ. It is also useful for testing MINTEQ after its implementation on a different computer because it utilizes many of the options in MINTEQ. The complete listing of output results is given in Appendix B. A listing of the MINTEQ input file is given in Appendix C.

MEXAMS IMPLEMENTATION TEST CASE

The sample problem for testing the MEXAMS system simulated the effect of loading the chemical benzo(f)quinoline into a seven compartment eutrophic lake. Benzo(f)quinoline is in the toxic chemical database, TOXCHEM.DAT and the eutrophic lake is described in the canonical environment database, CANON.ENV. For the MEXAMS test case, cadmium was modeled with the same

Loading and eutrophic lake environment as in the original EXAMS sample problem. However, instead of using the chemical, benzo(f)quinoline, the heavy metal option was selected from the toxic chemical database. The effect of this option is to bypass the chemistry computations in EXAMS allowing MINTEQ to determine the distribution of cadmium in dissolved, precipitated, or adsorbed forms for each compartment. EXAMS is thus reduced to a model of physical transport, i.e., advection and dispersion. Table 21 is a listing of the EXAMS input data.

For the purposes of this example the littoral and epilimnetic compartments (1,3,6) were assigned a higher pH than the benthic and hypolimnetic compartments (2,4,5,7). This provides an example of assigning different MINTEQ eater quality data to EXAMS compartments. The concentrations of major cations and anions in the MINTEQ water quality data was assumed to be the same as averaged values for Lake Mendota, Wisconsin, published by Hoffman and Eisenreich (1981). These values are given in Table 22.

The initial concentration of cadmium was set at 0.02 mg/ℓ merely to initialize the MINTEQ arrays. Appendix E presents an example of using MISP to create the MINTEQ input data and an example of using MISP in the MINTEQ-EXAMS mode for this test case. Appendix B gives a complete listing of the MISP, EXAMS and MINTEQ output.

MEXAMS RESOURCE REQUIREMENTS

MEXAMS has been implemented on a DEC PDP 11/70 using FORTRAN IV-PLUS/IAS, VERSION 3.0. FORTRAN IV PLUS is an extended FORTRAN based on ANS FORTRAN X3.9-1966. The following is a list of the PDP-11 FORTRAN IV extensions of the standard which are used in MEXAMS.

TABLE 21. SAMPLE EXAMS INPUT DATA

```
HVM
EOL
    5
    1 0.500         0.16  6.4000E-03        0.        0.
    2         0.        0.        0.        0.      0.02
    3         0.        0.    0.0320        0.        0.
    6         0.     0.166.4000E-03         0.        0.
    7         0.        0.        0.        0. 2.000E-02
HVM
HEAVY METAL
0 0 0 0 0
EOL
EUTROPHIC LAKE, AERL DEVELOPMENT PHASE TEST DEFINITION
    7
L
B
E
H
B
L
B
 40.00
 1.500     0.0000     2.000     0.0000     0.0000     1.500     0.0000
0.2500E+06 2500.    0.2500E+070.2500E+070.1250E+050.2500E+06 2500.
0.5000E+050.5000E+050.2500E+060.2500E+060.2500E+060.5000E+050.5000E+05
 5.000     0.5000E-01 10.00     10.00      0.5000E-01 5.000     0.5000E-01
 485.0     0.0000     0.0000     0.0000     0.0000     0.0000     0.0000
 40.00     0.0000     0.0000     0.0000     0.0000     0.0000     0.0000
 48.50     0.0000     0.0000     0.0000     0.0000     48.50     0.0000
 97.00     0.0000     0.0000     0.0000     0.0000     97.00     0.0000
0.0000      130.0     0.0000     0.0000      130.0     0.0000     130.0
 105.0
 5.000
0.8910E+110.3380E+120.1110E+130.2990E+130.5400E+130.8840E+130.1380E+140.1850E+14
0.2330E+140.2810E+140.5210E+140.1810E+150.2110E+150.2260E+150.2410E+150.2680E+15
0.2940E+150.3660E+150.5260E+150.6920E+150.7120E+150.6880E+150.6140E+150.9170E+15
0.9270E+150.9590E+150.9830E+150.9300E+150.9490E+150.1000E+160.1050E+160.1060E+16
0.1070E+160.1080E+160.1080E+160.1080E+160.1070E+160.1030E+160.9880E+15
 1.190     0.0000     1.190      1.190     0.0000     1.190     0.0000
 90.00     0.0000     85.00     0.0000     0.0000     90.00     0.0000
0.5000      1.850     0.5000     0.5000      1.850     0.5000     1.850
0.0000      137.0     0.0000     0.0000      137.0     0.0000     137.0
    7
    1    3    6    2    5    7    4
    3    6    0    1    4    6    3
 1.000      1.000      1.000      1.000      1.000      1.000      1.000
    6
    1    3    4    6    1    3
    2    4    5    7    3    6
0.5000E+050.2500E+060.2500E+060.5000E+05 2500.      2500.
 2.525     10.00      5.025      2.525     300.0      300.0
0.4676E-040.3985    0.9306E-040.4676E-04 1196.      1196.
0.3800E-010.3800E-010.3800E-010.3800E-010.3800E-010.3800E-010.3800E-01
 25.00      25.00      25.00      25.00      25.00      25.00      25.00
 25.00      25.00      25.00      25.00      25.00      25.00      25.00
 20.00      20.00      20.00      5.000      5.000      20.00      20.00
 8.000      6.500      8.000      7.400      6.500      8.000      6.500
 6.000      7.500      6.000      6.600      7.500      6.000      7.500
0.1000E-08            0.00.1000E-080.5000E-09           0.00.1000E-08        0.0
 51.00      250.0      2.200     0.7500      10.00      51.00      250.0
0.2000E-010.0000      1.000      1.000     0.0000     0.2000E-010.0000
 20.00      20.00      20.00      5.000      5.000      20.00      20.00


0.1000E+060.2000E+080.1000E+050.1000E+040.2000E+070.1000E+060.2000E+08
 1.000      1.000      1.000      1.000      1.000      1.000      1.000
 5.000     0.0000      10.00     0.0000     0.0000      5.000     0.0000
 2.000     0.0000      2.000      1.000     0.0000      2.000     0.0000
 2.500     0.0000      2.500     0.5000     0.0000      2.500     0.0000
0.4000E-020.0000     0.4000E-020.5000E-030.0000     0.4000E-020.0000
```

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TABLE 22. CONCENTRATIONS OF MAJOR CATIONS AND ANIONS FOR THE MEXAMS IMPLEMENTATION TEST CASE

Constituent	Concentration (mg/ℓ)
Ca^{2+}	29.04
Mg^{2+}	4.03
CO_3^{2-}	212.9
SO_4^{2-}	15.93
Cl^-	12.58

1. Mixed-mode arithmetic.
2. BYTE data type for character manipulation.
3. Direct-access unformatted input/output.
4. Comments at end of source lines.
5. OPEN and CLOSE file access control statements.
6. List-directed input/output.
7. INTEGER*4 (32 bit) data type.
8. ENTRY statement.
9. INCLUDE statement.

MINTEQ requires 64K bytes (overlaid) of memory, and 135K bytes of mass storage for utility files. The source code consists of about 4000 card images.

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APPENDIX A

MINTEQ PROGRAM LISTING

This appendix contains a complete listing of the PDP 11/70 version of MINTEQ.

Appendix A can be obtained by writing to the following address:

Environmental Protection Agency
Environmental Research Laboratory
College Station Road
Athens, Georgia 30613

APPENDIX B

TEST CASE RESULTS

This appendix contains complete listings of the MINTEQ output for the sea water and river water test cases as well as MISP, EXAMS and MINTEQ outputs for the MEXAMS implementation test case.

Appendix B can be obtained by writing to the following address:

Environmental Protection Agency
Environmental Research Laboratory
College Station Road
Athens, Georgia 30613

APPENDIX C

DESCRIPTION OF THE MINTEQ INPUT FILE

This appendix describes how to setup the sample description file for running the VAX and PDP 11/70 versions of MINTEQ. A detailed description of the options available to the user accompanies the file descriptions. Examples of MINTEQ input files are included.

The sample description file is broken into three sections. Each section is separated by a blank line. There should be three and only three blank lines in the sample file. The three sections will be called Basic Input Data, Type Modifications and insertion of Species. The format field designations for each line are given in parentheses following the line designation.

Section 1 - Basic Input Data

Line 1 (A80). Alphanumeric description of the sample.

Line 2 (A80). Alphanumeric description of the sample.

Line 3(a). Water temperature, analytical units and fixed ionic strength designation

---

(a) This line is free formatted on the VAX version.

The water temperature in degrees Celcius is entered followed by the analytical units. In the VAX version, the temperature and units must be separated by a space and the units enclosed in quote marks. The PDP 11/70 version follows the designated format fields. The analytical unit designations can be either 'PPM', 'MG/l', 'MOL', or 'MEQ/L'. These designations stand for parts per million, milligrams per liter, molality and milliequivalents per liter, respectively. The fixed ionic strength is entered following the analytical units. In the VAX version there must be a space between the analytical units and the ionic strength. The PDP 11/70 version follows the format fields. If the ionic strength is not fixed, enter 0.0 following the analytical units.

Line 4[8(I1,IX)]. This line contains the run specific user options.

Option 1. The inorganic carbon input option.

(0) = Total inorganic carbon
(1) = Total alkalinity

Option 2. The Debug print option. This is generally used only when modifications have been made to the code and the values of certain arrays must be checked.

(0) = No Debug printout.
(1) = Prints the values of the IDX, C, IDY, GAMMA, C and Y arrays

(3) = Prints the NNN, NN(1), NN(2) and the IDY, GK, GK1 arrays in subroutine KCORR.

(4) = Prints the IDX, X, IDY, L and GK arrays every iteration in subroutine SOLID and the saturation index for the solid added to the phase assemblage in subroutine SOLIDX.

Option 3. The charge balance option.

(0) - Terminates execution of the program if the initial charge in balance is greater than 30 percent.

(1) - Does not terminate execution regardless of the initial computed charge imbalance.

Option 4. Considered solids and print option.

(0) - Do not allow all of the solids in the data base to precipitate or dissolve. The only solids considered will be those entered in the next input section under type changes. Print the problem results after the initial aqueous speciation plus solids problem is solved and after all type V solids are either in equilibrium or undersaturated.

(1) - Allow all solids in the data base to precipitate if they become oversaturated. That is, designate all solids in the data base as Type V. Print the problem results only after the entire problem has been solved.

(2) - Consider all solids in the data base. Print the problem results after the initial user specified problem has been

solved and again after all Type V solids are undersaturated or in equilibrium.

(3) - Consider all solids in the data base. Print the problem results following the selection of every solid and after all of the solids are in equilibrium or undersaturated.

Option 5. The total number of iterations option.

(0) - Allow 40 iterations.

(1) - Allow 10 iterations.

(2) - Allow 100 iterations.

(3) - Allow 200 iterations.

The 100 or 200 iteration options should be selected if a large number of solids have been designated as considered solids. The ten iteration option is only useful when debugging the program.

Option 6. The pH variation option.

(0) - Do not allow the pH to automatically vary during precipitation/dissolution of solid phases.

(1) - Allow the pH to vary during precipitation/dissolution of solid phases. Not for this option to work all solid phases must be declared Type V in the initial input.

Option 7. The fixed ionic strength option.

(0) - Allow MINTEQ to compute the ionic strength.

(1) - Fix the ionic strength at the value designated on line 3.

Option 8. The numerical method option.

(0) - Use only Newton-Raphson iteration.

(1) - Use a combination of Newton-Raphson and a modified line search. This option should only be used after consulting the technical manual.

Option 9.(a) Output Option

(0) - Do not print on initial listing of the thermodynamic data.

(1) - Print a listing of the thermodynamic data.

Line 5 [I1,1X,4(F6.2,1X)]. This line is for input of adsorption parameters other than the mass total and activity guesses. The first parameter on this line is the adsorption model being used (I1 field). The options are:

0 - No Adsorption,

1 - Activity Kd, Langmuir isotherm, Freundlich isotherm,(a)

2 - Constant Capacitance Double Layer Model,

3 - Triple Layer Site Binding Model.

The next four inputs on this line are:

- Solid Concentration (g/l),
- Specific Surface Area (m^2/g),
- Inner Layer Capacitance (F/m^2),
- Outer Layer Capacitance (F/m^2),

(a) Available only on the VAX version.

input in this order. None of the last four inputs are required for the activity Kd. The constant capacitance model does not require an outer layer capacitance. The triple layer model requires all four data inputs.

Line 6+ (I7,IX,E9.3,IX,F6.2). Component input lines. There are as many of these lines are there are components. A blank line must follow the last component.

The first specification (I7) is the component ID number. Component ID numbers are given in Table 3. The second specification (E9.3 field) is the total analytical mass in the units designated on line 3. The only exception occurs when the constant capacitance or triple layer models are used. In such cases the analytical mass for the surface sites (SOH1 or SOH2 components) must be specified in sites per gram. The third specification on this line is a guess at the log of the component activity. If you leave this field blank the initial estimate of the activity will be the analytical molality divided by 100. Remember you need one line for every component and a blank line after the last component.

Section 2 - Type Modifications

This section is for changing the default species designations. The default type specifications have been described in Section 5.

The first line of this section contains the first species type designation and the number of species of this type Format (I3, 1X, I3). The type designations can range from two to six. Then for each species of the entered type a line is included (I7, 1X, E9.3, 1X, F6.2) designating information for that species. The first field specification is for the species I.D. number. Species I.D. numbers for components (Type I) are given in

Table 3. All other species I.D. numbers can be found in the listing of Thermodynamic Data given in the MINTEQ Technical Report. The next two specifications are for the new log K and enthalpy of reaction. These are both optional and if not included the default values in the thermodynamic data base are used. A blank line also ends this section. In the case of Type IV species with an initial mass total (in moles/ℓ) there is an additional input field for the initial mass. This input field follows the input of the enthalpy of reaction resulting in four inputs on one line. The input format for Type IV species is (I7, 1X, E9.3, 1X, F6.2, 1X, E10.3). For examples of necessary species modifications to solve specific problems see Section 5.

Section 3 - Insertion of Species Not in the Data Base

The first line is for designating the species type and the number of new species of this type (Format I3, 1X, I3). The species type can only range from two to six. The next lines contain the data for the new species of the specified type. There are three lines for each species. The first line of species data is in Format (I7, 1X, A12, 2F10.4, 2F8.3, 3F5.2, F9.4). The format fields correspond to the following data: I.D. number, name, enthalpy of reaction, log K, minimum log K, maximum log K, charge, Debye-Huckel A parameter, Debye-Huckel B parameter and molecular weight respectively. Only the ID number and log K are absolutely essential. For a description of the Debye-Huckel parameters see the MINTEQ Technical Report. The second line of data is in Format [F5.2, 1X, I1, 1X, 6(F7.3, 1X, I3, 1X)]. The format fields correspond to: carbonate alkalinity factor, number of components in the reaction and the stoichiometry and ID number for up to six components. The carbonate alkalinity factor is only useful if the input inorganic carbon is an alkalinity value. A description of the carbonate alkalinity factor is given in the MINTEQ Technical Report. The third line is in Format [3(F7.3, 1X, I3, 1X)] and is merely a continuation of the component entries for the inserted species. In the VAX version, the third line is in format [3(F7.3, 1X, I3, 1X), I1, 3 (F7.3, 1X, I3, 1X)]. The format field beginning with I1 is for inserting species informaton into the "B" matrix. Such information is only useful when the component stoichiometries in the mass action expressions are different from the stoichiometries in the mass balance equation. The latter format fields correspond to the number of components in the "B" matrix, stoichiometry of the component and component I.D. number. This section is also terminated with a blank line.

There occasionally can be a problem with determining species ID numbers for inserted species. The problem is that an ID number may be selected that matches an ID number already in the data base. The problem is usually in determining the last digit for aqueous species and the last two digits for minerals and solids since these are arbitrary designations. Table C-1 gives the highest ID numbers for aqueous species and Table C-2 gives the highest ID numbers for minerals and solids. To obtain the correct ID number first determine the first six digits for aqueous species and the first five digits for solids (see Section 5). The last digits can then be any values higher than those in Tables C-1 or C-2. Tables C-3 and C-4 give examples of the input data file.

TABLE C-1. HIGHEST I.D. NUMBERS OF AQUEOUS COMPLEXES

First Six Digits	Last Digit	First Six Digits	Last Digit	First Six Digits	Last Digit	First Six Digits	Last Digit	First Six Digits	Last Digit	First Six Digits	Last Digit
020130	2	160130	1	281141	0	460140	1	600130	1	900330	0
020141	0	160140	1	281142	0	460270	0	600140	2		
020142	0	160141	0	281180	2	460330	0	600180	3	901330	4
020180	3	160142	0	281270	2	460580	2	600270	3	901732	0
020270	0	160180	3	281330	5	460732	0	600330	5		
020330	1	160270	1	281580	1			600380	1	902180	0
020380	3	160330	4	281732	1	470002	1	600492	0	902270	3
020491	0	160380	1			470140	0	600730	1	902330	1
020492	0	160492	0	330060	2	470180	2	600732	1	902732	0
020730	4	160730	3	330061	3	470270	0				
020732	0	160732	1	330090	0	470330	1	731730	4	903002	7
				330140	1	470492	0			903270	3
030270	3			330141	0	470732	0	770270	0	903330	3
030330	3	230180	1	330142	0					903492	0
030732	1	230730	1	330270	2	490732	0	800330	0	903732	1
				330490	0						
090270	3	231140	2	330580	1	500140	1	891180	0	950130	1
		231141	0	330730	1	500270	0	891270	5	950140	2
100330	0	231142	0	330732	0	500580	0	891330	5	950180	4
		231180	3	330770	1	500732	0	891580	3	950270	0
150140	1	231270	0					891732	1	950330	3
150270	0	231330	4	410580	0	540130	0			950380	1
150330	0	231730	0	410732	0	540140	2	893140	2	950730	1
150580	2	231732	0			540180	1	893180	0	950732	1
150732	0			440732	0	540270	0	893270	3		
		280330	1			540330	2	893330	2		
		280580	1			540732	1	893580	4		
		280730	1					893732	1		
		280732	0					893770	0		

TABLE C-2. HIGHEST I.D. NUMBERS OF MINERALS AND SOLIDS

First Five Digits	Last Two Digits	First Five Digits	Last Two Digits	First Five Digits	Last Two Digits	First Five Digits	Last Two Digits	First Five Digits	Last Two Digits	First Five Digits	Last Two Digits
00020	00	20900	00	41470	00	50280	00	60800	00	73020	02
00060	00	20901	00	41500	00	50460	03	60902	00	73150	03
		20902	00	41600	04	50470	00	60950	06	73280	00
10020	00	20950	06	41900	00	50500	01			73460	02
				41901	01	50540	00	70020	00	73470	00
10160	01	30060	01	41902	00	50600	03	70100	00	73490	00
		30061	00	41903	00	50800	00	70150	02	73500	02
10230	03	30100	00	41950	02	50893	00	70160	00	73600	01
10231	02	30150	01			50950	01	70231	00		
10280	03	30230	00	42020	00			70231	01	80150	00
10470	00	30231	00	42100	00	51231	00	70280	01	80460	00
10540	00	30280	00	42150	00	51893	03	70281	00	80540	00
10600	01	30281	01	42160	00	51950	00	70410	00	80600	00
10731	00	30410	00	42230	00			70460	00	80950	00
10900	00	30440	00	42231	01	52160	00	70470	01		
10950	02	30470	00	42600	00	52600	00	70490	00	82150	01
		30471	00	42800	00	52950	00	70500	00	82160	00
		30600	01	42902	00			70540	00	82460	00
20020	00	30891	01	42950	00	60020	00	70600	07	82600	00
20030	03	30901	01			60030	01	70800	00	82950	00
20160	02	30902	02	43020	00	60100	00	70891	00		
20230	00	30903	00	43060	00	60150		70893	01		
20231	02						01	70902	00		
20281	02			43160	00	60160	05	70950	00		
20460	00	40020	00	43230	00	60230	00			84150	03
20470	03	40160	00	43600	00	60231	05	72030	00	84500	03
20471	00	40230	00	43950	00	60280	00	72100	00		
20540	01	40600	01			60281	01	72150	00	86030	02
20600	05	40950	00	50020	00	60410	02	72231	00	86280	00
20770	04			50100	00	60460	00	72281	00	86410	01
20891	01	41020	00	50150	03	60470	00	72470	00	86460	04
20893	03	41160	03	50160	00	60471	00	72540	00		
		41230	00	50231	02	60500	02	72600	00		
		41231	01			60540	02	72950	00		
		41281	00			60600	04				

TABLE C-3. MINTEQ INPUT DATA FOR THE SEAWATER TEST CASE

```
THIS IS THE SEAWATER TEST CASE PUBLISHED IN NORDSTROM ET AL.(1979)
ONLY THE THIRTY MOST IMPORTANT COMPONENTS WERE MODELED.
25.0  MG/L  0.00
1 0 0 0 0 0 0 0
0   0.00   0.00   0.00   0.00
    150 4.219E+02 -2.00
    460 1.321E+03 -1.00
    500 1.102E+04 -1.00
    410 4.084E+02 -3.00
    180 1.9805E+4 -1.00
    732 2.775E+03 -2.00
    140 7.129E+01 -3.00
    800 8.330E+00 -5.00
    090 2.598E+01 -5.00
    770 7.004E+00 -5.00
    270 1.423E+00 -6.00
    100 2.050E-02 -6.00
    580 6.140E-02 -7.00
    492 2.968E-01 -5.00
    490 3.070E-02 -5.00
    281 2.050E-03 -6.00
    280 0.000E-00 -10.0
    470 2.050E-04 -9.00
    030 2.050E-03 -9.00
    950 5.014E-03 -9.00
    160 1.020E-04 -10.0
    600 5.120E-05 -10.0
    231 7.160E-04 -10.0
    230 0.000E-00 -12.0
    540 1.740E-03 -10.0
    020 4.090E-05 -15.0
    061 7.749E-04 -12.0
    330 0.000E-00 -8.22
    001 0.000E-00  8.45

  3   4
    330       8.22
      1      8.446
2812800
2302310
```

TABLE C-4. MINTEQ INPUT DATA FOR THE RIVER WATER TEST CASE

```
RIVER WATER TEST CASE, PE COMPUTED FROM FE+2 AND FE+3,LOG PCO2 SET
AT -3.5 ATM,ACTIVITY KD FOR CD,AND METAL CONCENTRATONS = 0.1 MG/L
9.50  MG/L    0.00
1 0 0 0 2 0 0 0
1    0.00    0.00    0.00    0.00
     500 1.200E+01 -4.00
     100 1.000E-01 -5.00
     410 1.400E+00 -6.00
     150 1.220E+01 -4.00
     460 7.500E+00 -5.00
     770 1.362E+01 -5.00
     140 3.698E+01 -6.00
     180 9.900E+00 -5.00
     732 7.700E+00 -5.00
     090 2.860E-01 -5.00
     270 1.000E-01 -5.00
     580 2.100E-01 -9.00
     492 8.980E-01 -4.00
     490 1.440E-01 -5.00
     280 1.500E-02 -6.00
     281 7.000E-04 -14.0
     030 5.000E-03 -10.0
     950 1.000E-01 -6.00
     160 1.000E-01 -6.00
     600 1.000E-01 -6.00
     231 1.000E-01 -7.00
     540 1.000E-01 -6.00
     020 1.000E-01 -7.00
     330 0.000E-00 -8.01
     001 0.000E-00  2.00
     990 0.000E-00  0.00

   3   4
     330      8.01
     990
2812800
3301403      21.66
   5  45
5023100
4223100
4223101
2023100
4123101
5123100
2023101
7023101
4195000
5095000
5095001
4295000
2095000
2095001
```

MINTEQ TABLE C-4. (contd)

```
2095002
2095003
2095004
5195000
6095000
5016000
4116000
4116001
4116002
4216000



2016000
2016001
7016000
6016004
5060000
4260000
6060003
2060004
5060003
7060006
5054000
2054000
7054000
6054001
4102000
5002000
4202000
7002000
6010000
4210000
5010000
   6  1
      1

   2  1
9901600 SOH-CD                     10.00
      2    1.00 160    1.00 990

   6  1
1007321 BASO4(A)                    9.04
      2    1.00 100    1.00 732
```

APPENDIX D

MISP PROGRAM LISTING

This appendix contains a complete listing of MISP.

Appendix D can be obtained by writing to the following address:

Environmental Protection Agency
Environmental Research Laboratory
College Station Road
Athens, Georgia 30613

APPENDIX E

EXAMPLE MISP RUNS

This appendix contains two example MISP runs. Both runs are for the MEXAMS implementation test case described in the Programmers Supplement.

The first run prepares a MINTEQ input file. The water quality data for this run are given in Table 22. Cadmium was given an arbitrary "activity" Kd and the pH was fixed at 9.

The second example is a MISP run in the MINTEQ-EXAMS mode. The EXAMS environment is a seven compartment eutrophic lake with different water quality conditions in the epilimnetic/littoral compartments than in the hypolimnetic/benthic compartments. File MENDOTA2.DAT was created by copying file MENDOTA.DAT created in the first example and changing the pH. Appendix C should be consulted for a description of how to prepare a MINTEQ input file without using MISP.

```
SCI>> RUN MISP
22:28:05
          WELCOME TO MEXAMS
 METALS EXPOSURE ANALYSIS MODELING SYSTEM
  BATTELLE-NORTHWEST LABORATORIES


YOU HAVE A CHOICE OF THE FOLLOWING MODELS.
1) EXAMS-ONLY MODEL WITHOUT MINTEQ
2) MINTEQ-ONLY MODEL WITHOUT EXAMS
3) MINTEQ-EXAMS MODEL


ENTER MODEL NUMBER. (I1) >2
DO YOU HAVE A MINTEQ FILE READY (Y/N)? >N

QUESTION #1: ENTER TITLE OF SIMULATION. >
THIS FILE CONTAINS SOME REPRESENTATIVE WATER QUALITY DATA FOR A EUTROPHIC

QUESTION #2: ENTER DESCRIPTION OF WATER BODY. >
LAKE. THE PH WAS ARBITRARILY SET TO 9.0 WITH AN ACTIVITY KD OF 1.0

QUESTION #3: SELECT DATA UNITS:-

MG/L
PPM
MOL
MEQ/L

>MG/L

QUESTION #4: ENTER TEMPERATURE (DEG. CENTIGRADE)

QUESTION #5: WILL THE IONIC STRENGTH BE INPUT?
 (Y/N) >N
QUESTION #6: DO YOU HAVE EITHER A MEASURED PH OR
VALUE FOR THE TOTAL H? (Y/N) >Y

ENTER SELECTION NUMBER.

1) PH ?
2) TOTAL H ?

>1


ENTER PH. >9.0

QUESTION #7: IF SOLIDS ARE SELECTED TO DISSOLVE  OR PRECIPITATE
DO YOU WANT TO ALLOW THE PH TO VARY? (Y/N)>N

QUESTION #8: DO YOU HAVE AN EH VALUE OR DO
YOU WANT TO ENTER THE ELECTRON AS A COMPONENT? (Y/N) >N

QUESTION #9: DO YOU HAVE A TOTAL ALKALINITY MEASUREMENT? (Y/N) >N

QUESTION #10: DO YOU HAVE A MEASUREMENT OF TOTAL INORGANIC CARBON? (Y/N) >Y

ENTER TOTAL INORGANIC CARBON IN UNITS OF MG/L   >212.9
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DO YOU WANT TO GUESS THE LOG OF THE CO3 ACTIVITY? (Y/N) >Y

ENTER THE LOG OF THE CO3 ACTIVITY. >-6.00

QUESTION #11: IF A LARGE NUMBER OF MINERALS WILL PRECIPITATE OR DISSOLVE,
OPTION 3 SHOULD BE USED IN THE FOLLOWING QUERY.
HOW MANY ITERATIONS WILL YOU ALLOW?

0) 40
1) 10
2) 100
3) 200

ENTER OPTION NUMBER. >0

QUESTION #12: DO YOU WANT TO OVERRIDE THE CHARGE BALANCE CRITERIA? (Y/N) >Y

IF THE ANSWER TO THE FOLLOWING QUESTION IS 'NO', THEN ONLY
SOLIDS IN SAMPLE DESCRIPTION WILL BE CONSIDERED.

QUESTION #13:  DO YOU WANT TO ALLOW ALL SOLIDS IN THE DATA BASE TO
PRECIPITATE IF THEY BECOME OVERSATURATED? (Y/N) >N

QUESTION #14: ENTER DEBUG OUTPUT OPTION NUMBER
**CAUTION - DEBUG OUTPUT WILL ONLY BE USEFUL IF YOU
ARE THOROUGHLY FAMILIAR WITH MINTEQ.

0) NO DEBUG
1) ALL ARRAYS EACH ITERATION
2) ALL ARRAYS IN ALKOR
3) LOGK ARRAYS IN KCORR
4) ALL ARRAYS IN SOLID AND SOLIDX

>0

IN ANSWERING THE NEXT QUESTION REMEMBER YOU SHOULD
ONLY USE THE MODIFIED LINE SEARCH IF A PREVIOUS
RUN HAS FAILED TO CONVERGE!

QUESTION #15: DO YOU WANT TO USE THE MODIFIED LINE SEARCH AND
NEWTON-RAPHSON ITERATION? > (Y/N) >N

QUESTION # 16: DOES YOUR SAMPLE CONTAIN AG          ? (Y/N) >N

QUESTION # 17: DOES YOUR SAMPLE CONTAIN AL          ? (Y/N) >N

QUESTION # 18A DOES YOUR SAMPLE CONTAIN H3ASO4      ? (Y/N) >N

QUESTION # 18B DOES YOUR SAMPLE CONTAIN H3ASO3      ? (Y/N) >N

QUESTION # 19: DOES YOUR SAMPLE CONTAIN H3BO3       ? (Y/N) >N

QUESTION # 20: DOES YOUR SAMPLE CONTAIN BA          ? (Y/N) >N

QUESTION # 21: DOES YOUR SAMPLE CONTAIN BR          ? (Y/N) >N

QUESTION # 22: DOES YOUR SAMPLE CONTAIN FULVATE     ? (Y/N) >N

QUESTION # 23: DOES YOUR SAMPLE CONTAIN HUMATE      ? (Y/N) >N

QUESTION # 24: DOES YOUR SAMPLE CONTAIN CA          ? (Y/N) >Y

ENTER THE TOTAL CA           >29.04

DO YOU WANT TO GUESS THE ACTIVITY OF CA          ? (Y/N) >N
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QUESTION # 25: DOES YOUR SAMPLE CONTAIN CD          ? (Y/N) >Y

ENTER THE TOTAL CD          >0.02

DO YOU WANT TO GUESS THE ACTIVITY OF CD         ? (Y/N) >N

QUESTION . 26: DOES YOUR SAMPLE CONTAIN CL          ? (Y/N) >Y

ENTER THE TOTAL CL          >12.58

DO YOU WANT TO GUESS THE ACTIVITY OF CL         ? (Y/N) >N

QUESTION # 27: DOES YOUR SAMPLE CONTAIN CS          ? (Y/N) >N

QUESTION # 28A DOES YOUR SAMPLE CONTAIN CU+2        ? (Y/N) >N

QUESTION # 28B DOES YOUR SAMPLE CONTAIN CU+1        ? (Y/N) >N

QUESTION # 29: DOES YOUR SAMPLE CONTAIN F           ? (Y/N) >N

QUESTION # 30A DOES YOUR SAMPLE CONTAIN FE+2        ? (Y/N) >N

QUESTION # 30B DOES YOUR SAMPLE CONTAIN FE+3        ? (Y/N) >N

QUESTION # 31: DOES YOUR SAMPLE CONTAIN I           ? (Y/N) >N

QUESTION # 32: DOES YOUR SAMPLE CONTAIN K           ? (Y/N) >N

QUESTION # 33: DOES YOUR SAMPLE CONTAIN LI          ? (Y/N) >N

QUESTION # 34: DOES YOUR SAMPLE CONTAIN MG          ? (Y/N) >Y

ENTER THE TOTAL MG          >4.03

DO YOU WANT TO GUESS THE ACTIVITY OF MG         ? (Y/N) >N

QUESTION # 35A DOES YOUR SAMPLE CONTAIN MN+2        ? (Y/N) >N

QUESTION # 35B DOES YOUR SAMPLE CONTAIN MN+3        ? (Y/N) >N
QUESTION # 36A DOES YOUR SAMPLE CONTAIN NH4+        ? (Y/N) >N

QUESTION # 36B DOES YOUR SAMPLE CONTAIN NO2-        ? (Y/N) >N

QUESTION # 36C DOES YOUR SAMPLE CONTAIN NO3-        ? (Y/N) >N

QUESTION # 37: DOES YOUR SAMPLE CONTAIN NA          ? (Y/N) >N

QUESTION # 38: DOES YOUR SAMPLE CONTAIN NI          ? (Y/N) >N

QUESTION # 39: DOES YOUR SAMPLE CONTAIN PO4         ? (Y/N) >N

QUESTION # 40: DOES YOUR SAMPLE CONTAIN PB          ? (Y/N) >N

QUESTION # 41A DOES YOUR SAMPLE CONTAIN TTL SULFATE ? (Y/N) >Y

ENTER THE TOTAL TTL SULFATE  >15.93

DO YOU WANT TO GUESS THE ACTIVITY OF TTL SULFATE ? (Y/N) >N

QUESTION # 41B DOES YOUR SAMPLE CONTAIN S           ? (Y/N) >N

QUESTION # 41C DOES YOUR SAMPLE CONTAIN TTL SULFIDE ? (Y/N) >N

QUESTION # 42: DOES YOUR SAMPLE CONTAIN H4SIO4      ? (Y/N) >N
QUESTION # 43: DOES YOUR SAMPLE CONTAIN SR          ? (Y/N) >N

QUESTION # 44A DOES YOUR SAMPLE CONTAIN UO2+2       ? (Y/N) >N

QUESTION # 44B DOES YOUR SAMPLE CONTAIN UO2+        ? (Y/N) >N

QUESTION # 44C DOES YOUR SAMPLE CONTAIN U+4         ? (Y/N) >N

QUESTION # 44D DOES YOUR SAMPLE CONTAIN U+3         ? (Y/N) >N

QUESTION # 45: DOES YOUR SAMPLE CONTAIN ZN          ? (Y/N) >N

QUESTION #46: DO YOU WANT TO CONSIDER ADSORPTION? (Y/N) >Y

 WHICH ADSORPTION ALGORITHM?

1) ACTIVITY KD,ACTIVITY LANGMUIR OR ION EXCHANGE
2) CONSTANT CAPACITANCE MODEL
3) TRIPLE LAYER SITE BINDING MODEL

 >1
WILL YOU BE CONSIDERING TWO DIFFERENT SURFACE SITES? (Y/N) >N

WILL YOU BE USING AN ACTIVITY KD? (Y/N)Y

HOW MANY ADSORPTION REACTIONS WILL YOU CONSIDER?>1

ENTER REACTION ID NUMBER. >9901600

ENTER REACTION NAME. >SO-CD+2

ENTER ACTIVITY KD (CANNOT BE ZERO OR NEGATIVE). >1.00
CHECK MEXAMS USERS GUIDE FOR COMPONENT ID.
ENTER ID NUMBER FOR ADSORBING COMPONENT. >160
ENTER ID NUMBER FOR SURFACE (IE 990 OR 991)>990

WILL YOU BE USING AN ACTIVITY
LANGMUIR ISOTHERM? (Y/N) N

WILL YOU BE CONSIDERING ION EXCHANGE REACTIONS?(Y/N)N

QUESTION #47: DO YOU WANT TO ENTER ANY REDOX REACTIONS? (Y/N) >N


QUESTION #48: DO YOU WANT TO INCLUDE GASES AT A
FIXED PARTIAL PRESSURE? (Y/N) >N

QUESTION #49:  DO YOU WANT ANY SOLIDS TO BE PRESENT REGARDLESS OF
HOW MUCH MAY DISSOLVE? (Y/N) >N

  *** TYPE 4 ENTRIES ***

QUESTION #50: DO YOU WANT TO INCLUDE SOLIDS WHICH
ARE ONLY ALLOWED TO DISSOLVE A SPECIFIED AMOUNT? (Y/N) >N

  *** TYPE 5 ENTRIES ***

QUESTION #51: ARE THERE ANY SOLIDS THAT YOU WILL
ALLOW TO PRECIPITATE IF THEY BECOME OVERSATURATED ?
 Y/N) >Y
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ENTER NUMBER OF SOLIDS. >6

ENTER SOLID I.D. NUMBER. >5016000

ENTER SOLID I.D. NUMBER. >4116000

ENTER SOLID I.D. NUMBER. >4116001

ENTER SOLID I.D. NUMBER. >2016001

ENTER SOLID I.D. NUMBER. >2016000

ENTER SOLID I.D. NUMBER. >6016003

DO YOU WANT TO CHANGE THE EQUILIBRIUM CONSTANT FOR
ANY SOLIDS YOU JUST ENTERED? (Y/N) >N

DO YOU WANT TO CHANGE THE ENTHALPY OF REACTION FOR
ANY SOLIDS YOU JUST ENTERED? (Y/N) >N

  *** TYPE 6 ENTRIES ***

QUESTION #52: ARE THERE ANY SPECIES YOU DO NOT
WANT TO CONSIDER DURING THE EQUILIBRIUM COMPUTATIONS? (Y/N) >N

QUESTION #53: DO YOU WANT TO CHANGE THE EQUILIBRIUM CONSTANT OR
HEAT OF REACTION FOR ANY SPECIES IN THE DATA BASE
WHICH THIS PROGRAM HAS NOT ALREADY CHANGED? (Y/N) >N

QUESTION #54: DO YOU WANT TO ADD SPECIES TO THE
DATA BASE FOR THIS RUN ONLY? (Y/N)>N

QUESTION #55: DO YOU WANT TO CHECK YOUR COMPONENT ENTRIES? (Y/N) >Y

*** COMPONENT ENTRIES ***

  I.D. COMPONENT        TOTAL       ACT. GUESS

  150  CA             0.29040E+02   0.00000E+00
  160  CD             0.20000E-01   0.00000E+00
  180  CL             0.12580E+02   0.00000E+00
  460  MG             0.40300E+01   0.00000E+00
  732  TTL SULFATE    0.15930E+02   0.00000E+00
  990  SOH1           0.00000E+00   0.00000E+00
ARE THERE ANY CHANGES? (Y/N) >N

SELECT RUN OPTION!

1) STORE DATA IN A FILE.
2) MODEL DATA.

 ENTER OPTION NUMBER >1

 ENTER FILE NAME. >MENDOTA.DAT
  TIME =    501.1854
TTOOB  --  STOP
```

App E

App E

```
SCI>> RUN MISP
22:39:12
         WELCOME TO MEXAMS
 METALS EXPOSURE ANALYSIS MODELING SYSTEM
  BATTELLE-NORTHWEST LABORATORIES


YOU HAVE A CHOICE OF THE FOLLOWING MODELS.
1) EXAMS-ONLY MODEL WITHOUT MINTEQ
2) MINTEQ-ONLY MODEL WITHOUT EXAMS
3) MINTEQ-EXAMS MODEL


ENTER MODEL NUMBER. (I1) >3
SELECT THE METAL ID FROM THE FOLLOWING TABLE.

      ID
      20  AG
      61  H3AS04
     160  CD
     231  CU+2
     540  NI
     600  PB
     950  ZN

>160

HOW MANY MINTEQ INPUT FILES WILL BE NEEDED? >2

ENTER NUMBER OF COMPARTMENTS FOR FILE  1 >3

ENTER COMPARTMENT NUMBERS FOR FILE  1
SEPARATE THE NUMBERS WITH A SPACE OR COMMA. >1,3,6

ENTER NUMBER OF COMPARTMENTS FOR FILE  2 >4

ENTER COMPARTMENT NUMBERS FOR FILE  2
SEPARATE THE NUMBERS WITH A SPACE OR COMMA. >2,4,5,7

HOW MANY TIMES DO YOU WANT TO USE MINTEQ TO
UPDATE THE STEADY STATE CONCENTRATION ? >2

HOW OFTEN DO YOU WANT TO USE MINTEQ FOR
PERSISTENCE COMPUTATIONS ?

SELECT OPTION NUMBER FROM THE FOLLOWING LIST.

1)  EVERY TIME
2)  EVERY OTHER TIME
3)  EVERY THIRD TIME
4)  EVERY FOURTH TIME
5)  EVERY FIFTH TIME
6)  NO PERSISTENCE UPDATE

>5

SELECT MINTEQ OUTPUT OPTION!

1) FULL MINTEQ PRINTOUT.
2) AQUEOUS SPECIES DISTRIBUTION AND ALL MASS TOTALS.
3) ALL MASS TOTALS
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```
ENTER NAME OF MINTEQ INPUT FILE  1 >MENDOTA.DAT
MENDOTA.DAT
ENTER NAME OF MINTEQ INPUT FILE  2 >MENDOTA2.DAT
MENDOTA2.DAT
ENTER NAME OF EXAMS INPUT FILE >EXAMS.DAT
EXAMS.DAT




 WAITING FOR EXAMS
  TIME =     35813.16
BEXAMS  --  STOP

TTOOA  --  STOP

  TIME =     128.1161
TTOOB  --  STOP


SCI>>




     LOGO
COMMAND NOT ALLOWED - ACTIVE TASK

SCI>> AB

SCI>> LOGO
User RSA  UIC [220,7] TT00: 22:41:59  7-JUN-83
22:41:59 END PDS RSA TT00:


BYE
```